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CLASSIFICATION OF THE NATURAL SILICATES*

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INTRODUCTION

Many efforts have been made in the past to interpret the chemical constitution of the silicates, but views concerning them long remained largely subjective. The more recent development of the *x*-ray analysis has cast new and important light upon this problem. We have thought that a summary of the results bearing upon the chemical constitution and composition of the natural silicates, obtained by the various workers in this field, would be welcomed by the student.

We will deal first with the classification of the silicates as a basis for the presentation of the data assembled. In the second part we will give tables showing their composition.

PART I. CLASSIFICATION OF THE SILICATES

I. BASIS OF CLASSIFICATION

Underlying principles. We will first consider certain principles which must underlie any sound classification of the silicates. There are three chief principles.

The first is that of ionic radii. The first determination of the radii of ions was made by W. L. Bragg and published by him in 1920.[1] His measurements, though inaccurate, were valuable since they suggested new and important principles. The first accurate measurements were made by J. Wasastjerna,[2] who determined the radii of O and F ions by the refractive indices of their compounds. V. M. Goldschmidt[3] continued the investigation and prepared tables giving the radii of ions of numerous other elements. Later discussions by L. Pauling,[4] V. M. Goldschmidt,[5]

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* Read before a joint session of the Mineralogical Society of America and the Geological Society of America, Dec. 30, 1936.

[1] Bragg, W. L., *Phil. Mag.*, vol. **40,** p. 169, 1920. See also *Phil. Mag.*, vol. **2,** p. 258, 1926.

[2] Wasastjerna, J., *Soc. Scient. Fenn.*, Comm. I, p. 38, **1923**. (*Finska Vetenskaps—Societeten Commentationes Physico—Math.*)

[3] Goldschmidt, V. M., Geochemische Verteilungsgesetze der Elemente: *Skrifter det Norske Videnskaps-akad., Oslo, I, Matem-Naturvid Klasse*, Pt. VII, **1926,** No. 2.

[4] Pauling, L., *Jour. Am. Chem. Soc.*, vol. **49,** p. 765, 1927.

[5] Goldschmidt, V. M , Krystallchemie: *Fort. Min. Kryst. Petrog.*, vol. **15,**, p. 73, 1931.

W. H. Zachariasen[6] and others[7] have added greatly both to the accuracy of the measurements and to our knowledge of the subject.

The fundamental principle that atoms replace each other in isomorphous structures, not as long supposed, according to their chemical relations, but according to the radii of their ions, was first suggested by F. Zambonini[8] in 1922 and E. T. Wherry[9] in 1923. It was later developed more fully by V. M. Goldschmidt,[10] W. L. Bragg[11] and others. It may be termed Zambonini's Law.

The second principle, announced by L. Pauling,[12] affirms that the sum of all electrostatic charges is zero, not only in larger units, but in all adjacent parts of the structure, otherwise instability would result.

The third principle concerns more particularly the constitution of the silicates and is highly important. It was established by W. L. Bragg[13] and his co-workers and confirmed by others.

It was shown that SiO_4 groups occur in all the natural silicates, however varied their composition. These groups are in the form of tetrahedra, the four large O atoms occupying the solid angles of each tetrahedron and the small Si atom being found in its center.[14] (The apices of the solid angles of the tetrahedron are placed at the centers of the O atoms.)

It has been shown further that the tetrahedra combine by their solid angles, one oxygen atom being shared equally by two adjoining tetrahedra. *It is very important to recognize that the tetrahedra do not combine by their edges or faces, but by their solid angles only.* All the varied and complex compositions of the silicic acids are shown to be formed by the combinations of the SiO_4 tetrahedra in this manner.

Development of types. Since all the various silicates are thus made, it is possible to develop all conceivable types of silicates by considering the various ways in which the tetrahedra may combine by their solid angles. There are five such types.

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[6] Zachariasen, W. H., *Zeits. Krist.*, vol. **80**, p. 137, 1931.

[7] Neuburger, M. C., *Zeits. Krist.*, vol. **93**, pp. 1–36, 1936, table.

[8] Zambonini, F., *Rend. Accad. Lincei*, vol. **31**, p. 295, 1922. Synopsis in *Am. Mineral.*, vol. **8**, p. 81, 1923.

[9] Wherry, E. T., *Am. Mineral.*, vol. **8**, p. 1, 1923.

[10] Goldschmidt, V. M., *op. cit.*, No. 2, **1926.**

[11] Bragg, W. L., West, J., *Proc. Roy Soc.*, A, vol. **114**,, p. 450, 1927.

[12] Pauling, L., *Am. Chem. Jour.*, vol. **51**, p. 1010, 1929.

[13] Bragg, W. L., West, J., *Proc. Roy. Soc.*, A, vol. **114**, p. 450, 1927.
Bragg, W. L., *Proc. Roy. Inst.*, vol. **25**, p. 302, 1927. *Zeits. Krist.*, vol. **74**, p. 237, 1930.

[14] This was first shown by Sir Wm. Bragg and R. E. Gibbs in β Quartz (*Proc. Roy. Soc.*, A, vol. **109**, p. 405, 1925), and later extended to silicates in general by W. L. Bragg and his associates.

1. Tetrahedra uncombined.
2. Tetrahedra combined by one solid angle.
3. Tetrahedra combined by two solid angles.
4. Tetrahedra combined by three solid angles.
5. Tetrahedra combined by four solid angles.

Since a tetrahedron possesses only four solid angles it is manifest that this process can go no further and hence, that there are but five fundamental types.

II. Fundamental Types

Let us consider the characteristics of these types. (See Fig. 1.)

Fig. 1. Table Showing Relations of the Fundamental Types

Fundamental Silicate Types

Type	Name	Chemical Formula	Solid angles combined in SiO_4 groups	Geometric form	Valence and O per Si
I	Orthosilicates	R'_4SiO_4	none	Separate tetrahedra	$''''SiO_4$
II	Orthodisilicates	$R'_6Si_2O_7$	1	Pairs	$'''SiO_{3\frac{1}{2}}$
III	Metasilicates	R'_2SiO_3	2	Chains—rings	$''SiO_3$
IV	Metadisilicates	$R'_2Si_2O_5$	3	Sheets	$'SiO_{2\frac{1}{2}}$
V	Dioxide type	SiO_2	4	Net-works	SiO_2

Complex Silicate Types

Made by association of two or more fundamental types in the same crystal.

1. The simplest type is manifestly one in which the SiO_4 tetrahedra remain separate and are not combined with others. The body in question is evidently an orthosilicate. Its formula is R'_4SiO_4, since the valency of the SiO_4 group is four. This type may be best defined as having tetrahedra with their solid angles uncombined. The structure is illustrated by the projection of olivine in Fig. 2.

2. The first step in combination is where two SiO_4 tetrahedra unite to form a pair. This they do by joining solid angles, one oxygen atom being shared equally by two neighboring tetrahedra. The formula of such compounds is $R'_6Si_2O_7$, instead of $R'_8Si_2O_8$ as in the case of the original two tetrahedra. The valency of the pair is six, their being six oxygen atoms free to unite with neighboring kations. It is clearly an orthodisilicate. The structure of this type is illustrated in Fig. 3.

3. The union of the SiO_4 groups by two solid angles produces an endless series of tetrahedra. This may take the form either of endless chains, or it may be curved to form rings. In either case the formula is $R_2' SiO_3$. It is a metasilicate with a valency of two. The structure of forms having chains is illustrated in Fig. 4, those with rings in Fig. 5.

4. The SiO_4 tetrahedra may unite by three solid angles to produce sheets of indefinite extent. One solid angle of each group remains free in this case. The free angles may turn in either direction, or all may

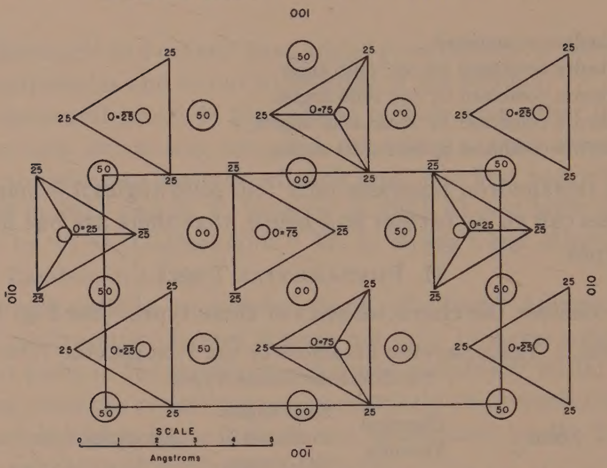

FIG. 2. Type I, Orthosilicates. Projection of olivine[15] upon the (100) plane, based upon the work of W. L. Bragg and G. B. Brown, (*Zeits. Krist.*, vol. **63**, p. 538, 1926. Compare Fig. 2, p. 545). The rectangle outlines the unit cell. The tetrahedra are shown by triangular outlines, their three-fold axes being parallel to the *a*-axis, their apices directed alternately towards and away from the observer. The small circles within the tetrahedra represent Si atoms, the larger circles (Mg, Fe) atoms. The parameters are on the *a* axis, the origin being at the center. The separate character of the SiO_4 tetrahedra, characteristic of this type, is well shown.

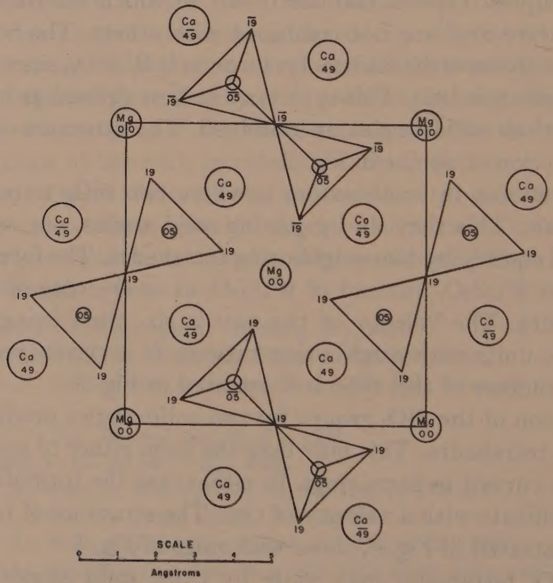

FIG. 3. Type II, Orthodisilicates. Projection of melilite (akermanite) upon the (001) plane, showing the union of tetrahedra by one solid angle to form pairs. Based upon the work of B. E. Warren (*Zeits. Krist.*, vol. **74**, p. 131, 1930. Compare Fig. 2, p. 135). The square outlines the unit cell. The small circles represent Si atoms. The parameters are on the *c* axis. The formula is seen to be Si_2O_7, and the valency 6 (since there are six free O atoms).

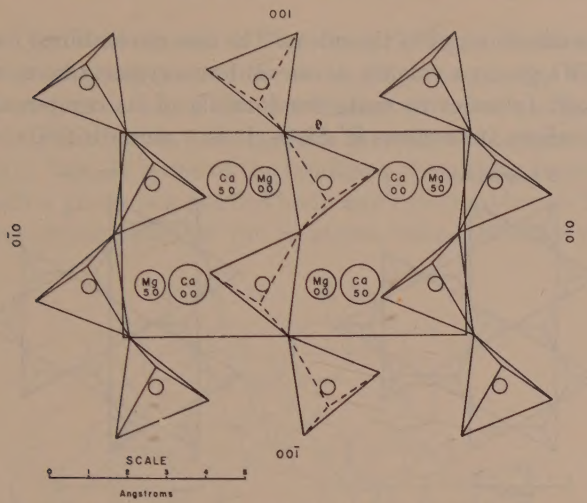

FIG. 4. Type III, Metasilicates. Projection of diopside, showing the union of SiO_4 tetrahedra by two solid angles to produce chains of indefinite extent. Based upon the work of B. E. Warren and W. L. Bragg.[16] The plane of projection is (100), the line of vision being parallel to the *a* axis. The front half, only, of the unit cell is projected. The formula is seen to be SiO_3, the valency 2, since there are two free O atoms in each tetrahedron.

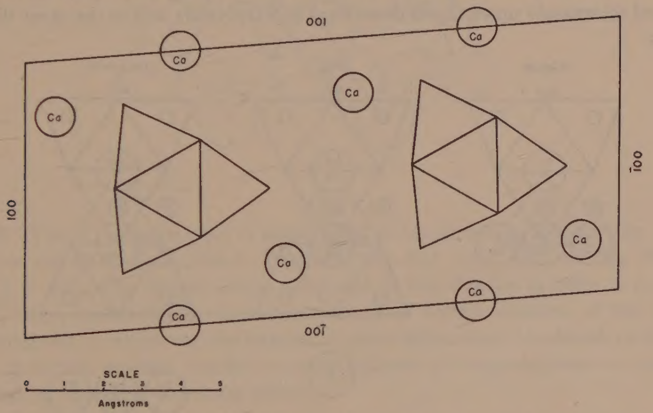

FIG. 5. Projection of monoclinic wollastonite on (010), after M. Barnick (Inaugural Dissertation, *Berlin*, Fig. p. 30, 1936). Chains formed of tetrahedra joined by two solid angles are curved to form rings.

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[15] The characteristics of the different types are illustrated in Figs. 2 to 8. The SiO_4 groups are represented as tetrahedra. The oxygen atoms are not shown in the drawings, save in Fig. 8. The centers of the oxygen atoms are located at the apices of the solid tetrahedral angles, their diameters being equal, approximately, to the length of the tetrahedral edges. The small circles in the centers of the tetrahedra represent Si or Al atoms. Double circles represent two atoms. All atoms are drawn to one-half true scale, to avoid crowding.

[16] The projection was calculated by the author from coordinates of the atoms, given by B. E. Warren and W. L. Bragg, *Zeits. Krist.*, vol. **69**, p. 189, 1928. Compare Fig. 9, p. 188. See also W. L. Bragg, *Zeits. Krist.*, vol. **74**, p. 252, Fig. 8, 1930.

turn in one direction, as in the micas. The one uncombined oxygen atom gives the SiO_4 group a valency of one and an oxygen: silicon ratio of two and one half. In order to write the formula of its compounds without fractional values, it becomes $R'_2Si_2O_5$. It is a metadisilicate. The struc-

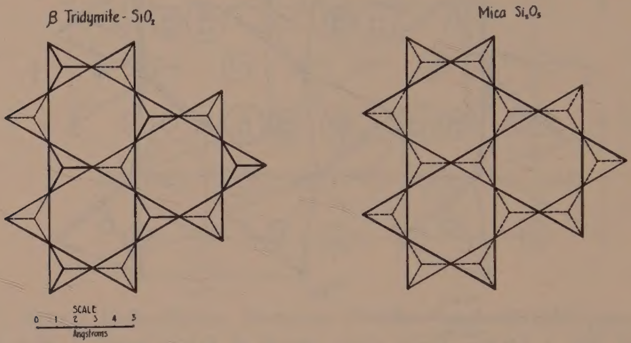

Fig. 6. Type IV, Metadisilicates. The fourth type is illustrated by Figs. 6 and 7, both of which are after L. Pauling, (*Proc. Nat. Acad. Sci.*, vol. **16**, p. 124, Figs. 2 and 3, 1930). In Fig. 6 the SiO_4 group of β tridymite (or β cristobalite) and $(Si,Al)O_4$ groups of mica are projected upon the basal pinacoid. The tetrahedra are united by three solid angles to form sheets of indefinite extent parallel to (001). The remaining free angles of the tetrahedra are directed alternately upward and downward in β tridymite and in the same direction in the micas.

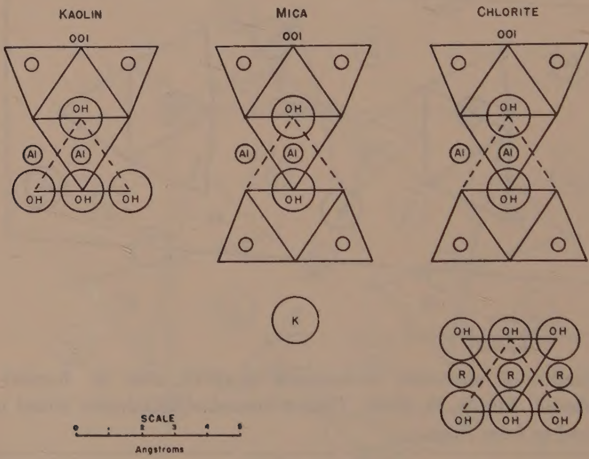

Fig. 7. Diagrammatic projection of members of the kaolin, mica and chlorite families, on a plane perpendicular to the basal pinacoid. Sheets of Si_2O_5, or $(Si, Al)_2O_5$, are seen to alternate with sheets of $Al_2(OH)_4$ in kaolin, $Al_2(OH)_2$ and K(or Na) in micas, and $Al_2(OH)_2$ and $R_3(OH)_6$ in chlorites. All show the sheet-like structure of these minerals.[17]

[17] Pauling, L., *Proc. Nat. Acad. Sci.*, vol. **16**, p. 578, Fig. 1 and p. 580, Fig. 2 (chlorites), 1930. The diagrams of Pauling show but one Al atom in the unit cell. A second Al atom has been added in these diagrams since two are present.

ture of this type is illustrated in Figs. 6 and 7. Figure 6 shows the Si_2O_5 sheets viewed perpendicular to the sheet, Fig. 7 parallel to the sheet.

5. The last step is where the tetrahedra unite with others by four solid angles. There are in this case no uncombined oxygen atoms and the formula is SiO_2. It is one of the familiar polymorphic forms of silicon dioxide. Such a group is a neutral body and can combine no further. If, however, we replace part of the Si atoms, found in some multiple of the group, by Al atoms, the charge of the whole becomes negative. The formula of such a body is $R(Al,Si)O_2$. Its valency equals the number of the replacing Al atoms. Such groups form three-dimensional net-works of indefinite extent. Figure 8 illustrates structures of this type.

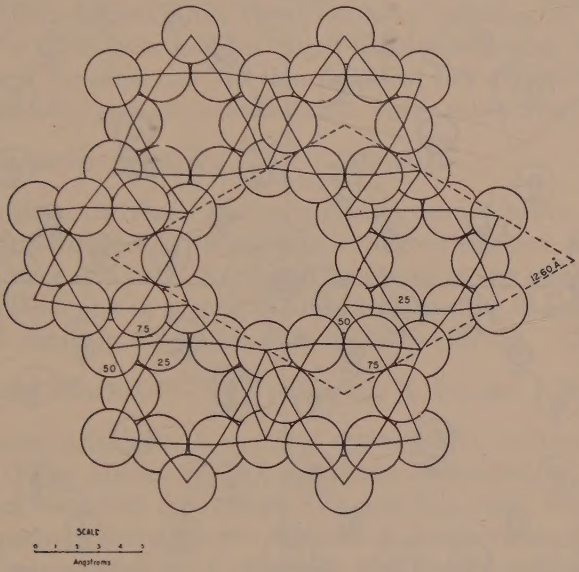

FIG. 8. Type V, Dioxide type. A single sheet of the structure of cancrinite is shown, projected on the (001) plane after L. Pauling (*Proc. Nat. Acad. Sci.*, vol. **16,** 1930. Compare Fig. 5, p. 458). The oxygen atoms are drawn in this diagram in order to show the remarkable, large, tunnel-like cavities characteristic of certain members of this type (e.g. the ultramarines) in which various kations or other anions may be placed, or even water retained, as in the zeolites. Similar successive sheets are superimposed to form three-dimensional net-works of indefinite extent.

The operations are clearly at an end. We have five fundamental types of silicates. *The structures thus developed are the same as those previously recognized, but their assembling into groups and the basis upon which they are developed are not the same.*

III. Complex Types

The classifications of the past have been based largely upon the geometric forms of the structure, but the subject is not so simple as has been assumed. The various fundamental types we have described may unite with each other to form complex assemblages. Just as, in chemical reactions, elements unite to form compounds, so the fundamental types may unite to produce complex types. The fundamental types may be compared to the elements, the complex ones to the compounds resulting from their union. As the chemical elements retain their identity in their compounds so each fundamental type retains its identity in the complex ones. Their characteristics are illustrated by Figs. 9, 10 and 11.

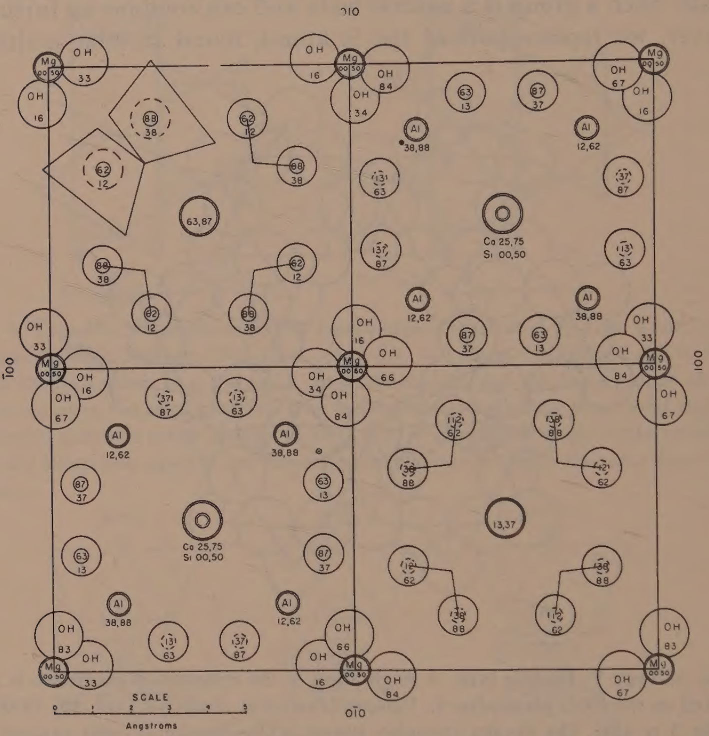

Fig. 9. Projection of vesuvianite on the (001) plane, after B. E. Warren and D. I. Modell, illustrating the characteristics of the complex silicates. Adjacent quadrants are seen to differ in both structure and composition. The SiO_4 tetrahedra are separate in the upper right- and lower left-hand quadrants of the projections: (the O atoms are omitted to avoid confusion of the eye). The SiO_4 tetrahedra are united by one solid angle to form pairs in the upper left- and lower right-hand quadrants. Only one pair is drawn, but the union of the others by a single 0 atom is represented. The small circles represent Si atoms, the larger, unlettered circles Ca atoms. The parameters are given on the c axis.

Vesuvianite, illustrated in Fig. 9, was studied by B. E. Warren and D. I. Modell.[18] They showed that the unit cells may be divided into quadrants of two quite different types. The diagonally opposite quadrants are alike and symmetrical with respect to a center of symmetry, but they differ fundamentally from the other quadrants of the unit cell. The authors showed further that the portion of the cell represented in the upper right-hand quadrant of Fig. 9 has essentially the structure and composition of an orthosilicate garnet, with separate tetrahedra. The portion represented in the upper left-hand quadrant of the figure, on the contrary, has its tetrahedra united to form pairs with the formula Si_2O_7. Parts of the same unit cell thus represent two different types, an orthosilicate, SiO_4, and an orthodisilicate, Si_2O_7, respectively. The formula of vesuvianite is $Ca_{10}Al_4\left|\begin{matrix}(SiO_4)_5\\(Si_2O_7)_2\end{matrix}\right| 2Mg(OH)_2$.

It is manifest, therefore, that vesuvianite cannot justly be put in either the orthosilicates, with separate, or orthodisilicates, with paired tetrahedra, since it is both. Nor can it be placed in any one division of any classification now in general use.[19] It is interesting to note that the types remain distinct, though found in the same unit cell.

Bertrandite, $Be_2(BeOH)_2\left|\begin{matrix}SiO_4\\SiO_3\end{matrix}\right.$ studied by T. Ito and J. West[20] illustrates the same principles. It contains separate SiO_4 tetrahedra associated with chains formed of SiO_4 tetrahedra combined by two solid angles, hence combined the formula SiO_4 and SiO_3. Like vesuvianite it cannot properly be placed in any division of classifications now in use.

Zunyite, was studied by L. Pauling, who showed that it contains groups of five tetrahedra, united by their solid angles as illustrated in Fig. 10.[21] The outer tetrahedra are joined to the central one by one solid angle and the central tetrahedron is united to the outer ones by four solid angles. The formula of the group, written without fractional values is, therefore, $\left|\begin{matrix}(Si_2O_7)_2\\SiO_2\end{matrix}\right.$. It is a three-dimensional group, but it cannot be referred to the recognized three-dimensional division, since the latter has groups of tetrahedra of indefinite ("infinite") extent. It cannot be placed with the finite, self-contained, pairs and rings, since the latter are one- or two-dimensional. It is manifest that it cannot be placed properly in current classifications. It is a complex silicate and consists of our types II and V in combination. Associated with the groups of five tetrahedra are also separate AlO_4 tetrahedra. If the latter be viewed as representatives of SiO_4 then zunyite has also an orthosilicate element.

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[18] Warren, B. E., Modell, D. I., *Zeits. Krist.*, vol. **78**, p. 422, 1931. Compare Fig. 4, p. 428.

[19] Machatschki, F., in 1932 proposed to unite all silicates having separate or finite groups of SiO_4 tetrahedra in his "Orthosilicates" division. Others have not followed him in this.

[20] Ito, T., West, J., *Zeits. Krist.*, vol. **83**, p. 384, 1932.

[21] Pauling, L., *Zeits. Krist.*, vol. **84**, p. 447, Fig. 2, 1933.

The formula of zunyite is $Al_{12}\left|\begin{array}{c}(Si_2O_7)_2\\ SiO_2\\ AlO_4\end{array}\right|(OH,F)_{18}Cl.$

Tremolite is another illustration of the complex silicates. It was studied by B. E. Warren.[22] One of the double chains, so characteristic

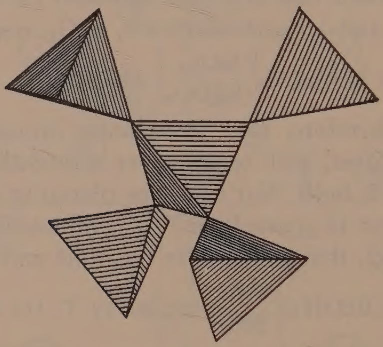

FIG. 10. A group of five SiO_4 tetrahedra of zunyite, after L. Pauling (*Zeits. Krist.*, vol. **84**, p. 447, Fig. 2, 1933). The tetrahedra are united by their solid angles to form a limited, three-dimensional group combining types II and V.

of the amphiboles, is shown in Fig. 11. It consists of pairs of tetrahedra alternating in sequence. The tetrahedra of the first pair are united to others by two solid angles and have altogether the formula Si_2O_6. They are succeeded by two tetrahedra united to others by three solid angles, hence with the formula Si_2O_5. It thus consists of two chains whose alternate links are united to produce incipient sheets and embraces in the same structure one-dimensional and two-dimensional elements of our types III and IV. Its general formula is $R'_6\left|\begin{array}{c}Si_2O_6\\ Si_2O_5\end{array}\right.$ which, in the case of tremolite, becomes $Ca_2Mg_5\left|\begin{array}{c}Si_4O_{12}\\ Si_4O_{10}\end{array}\right|(OH,F)_2.$

The last complex silicate to which we will refer is epididymite, described by T. Ito.[23] It is an interesting illustration of structures of this type. It was shown by Ito to consist of discontinuous sheets made of three-dimensional bands ("triple chains" of Ito). Its formula is $\mathrm{NaBeOH}\left|\begin{matrix}\mathrm{Si_2O_5}\\ \mathrm{SiO_2}\end{matrix}\right.$, comprising our types IV and V. It cannot be properly placed in any classification now in use.

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[22] Warren, B. E., *Zeits. Krist.*, vol. **72**, p. 42, 1929.

[23] Ito, T., *Zeits. Krist.*, vol. **88**,, p. 142, 1934.

It is manifest that the classifications of the past, based upon the geometric form, failed to provide a place for the complex structures we have described and for other similar ones. Moreover, no simple method is known for predicting the possible geometric structures. A classification based upon the manner in which the tetrahedra unite, on the contrary, remains valid, correctly expresses the chemical formulae and classifies the resulting geometric forms. It seems possible that there may be a much greater recognition of structures of complex types in the future.

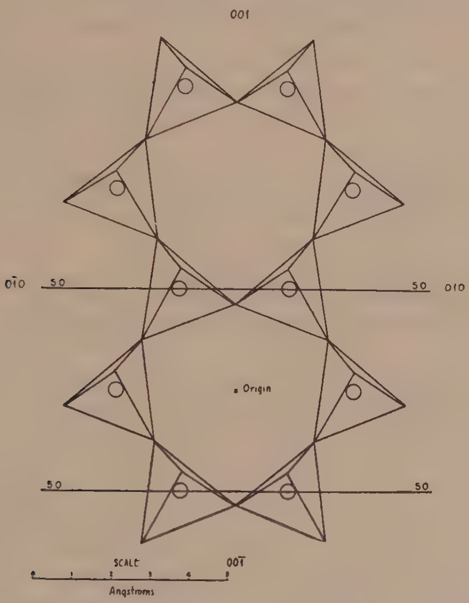

FIG. 11. Projection of a double chain of tremolite on the (100) plane, based on the work of B. E. Warren.[24]

IV. COMPARISON WITH CLASSIFICATION OF OTHERS

It seems desirable to present the relations of the classification here proposed to those that have been given by others, based upon x-ray study.

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[24] The projection was calculated by the author from coordinates given by B. E. Warren, *Zeits. Krist.*, vol. **72**, p. 52, 1929. Compare Fig. 1, p. 46 and Fig. 2, p. 48 (by error made diopside in original).

1. Classifications by Others

(a) *F. Machatschki*, 1928. The first classification upon this basis, with which I am acquainted, was proposed by Machatschki in 1928.[25] It seems to rest, in part only, upon *x*-ray investigations, but is singularly penetrating and suggestive. He recognized three types: an Orthotype, a Metatype and a Feldspar type, respectively.

His Orthotype comprised silicates with separate SiO_4 tetrahedra, agreeing, in this respect with the usage of most others. Later, however, he used the term for a very different assemblage. His Feldspar type comprised crystals built on the pattern of silicon dioxide in which the Si atoms are replaced, in part, by Al, the valency of the group equaling the number of replacing Al atoms. The characteristics of the various divisions are shown in the following table.

Orthotype. SiO_4 groups separate $(SiO_4)^{-4}$
Metatype. SiO_4 groups united by two O atoms, forming chains. $(SiO_3)^{-2}$
Feldspar type. SiO_4 groups united by four O atoms forming net-works. (SiO_2) type.

(b) *W. L. Bragg*, 1930. In 1930 Bragg added two new types[26] to the divisions proposed by Machatschki, with whose work he was acquainted. The first of these was his "Self-contained" group, consisting of bodies with tetrahedra united to form pairs, Si_2O_7, or rings, the latter in various multiples of SiO_3. The essential idea is that of a body containing a finite number of combining SiO_4 tetrahedra, in contrast with the infinite number found in his succeeding divisions. He adds, also, a second group of crystals having the structure of the micas, with indefinitely extended two-dimensional sheets and a general formula $R_2'Si_2O_5$ His classification is shown in the following table.

(a) Separate SiO_4 groups, Orthosilicates, $(SiO_4)^{-4}$.
(b) Self-contained groups, (SiO_4 groups limited).
  1. Pairs, $(Si_2O_7)^{-6}$. 2. Rings, $(Si_3O_9)^{-6}$, $(Si_4O_{12})^{-8}$, $(Si_6O_{18})^{-12}$.
(c) Silicon-oxygen chains.
  1. Single chains, $(SiO_3)^{-2}$, 2. Double chains, $(Si_4O_{11})^{-6}$.
(d) Silicon-oxygen sheets, $(Si_2O_5)^{-2}$.
(e) Three-dimensional net-works, $(Si,Al)O_2$.

Bragg's classification has justly had very great weight, not only because of the value of its suggestions, but also because of the brilliance of his investigations.

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[25] Machatschki, F., *Centrbl. Min.*, A, p. 98, **1928**.
[26] Bragg, W. L.. *Zeits. Krist.*, vol. **74**, pp. 300–301, 1930.

(c) In the same year, 1930, *St. v. Náray-Szabó* presented a new classification.[27] He accepted all of Bragg's divisions for what he terms his "Silicates proper," but adds to them new divisions under the name "Complex silicates." The latter are characterized by the presence of accessory anions in addition to the silicon oxides. In this manner he proposes eight new groups as follows:

1. Titano-silicates.
2. Boro-silicates.
3. Carbonato-silicates.
4. Vanado-silicates.
5. Sulphato-silicates.
6. Sulpho-silicates.
7. Three-dimensional networks.
8. Silicates with several anions, (e.g. Thaumasite, with SiO_3, CO_3, SO_4).

(d) *F. Machatschki*, 1932. In 1932 Machatschki offered a new and enlarged classification which has had much weight.[28] His divisions are:

A. Orthotype, embracing silicates with SiO_4 tetrahedra separate, or united to form pairs or rings; their formulae $(SiO_4)^{-4}$, $(Si_2O_7)^{-6}$, $(SiO_3)^{-2}$.

B. Metatype, SiO_4 tetrahedra united to form chains of indefinite extent, their formula $\infty\ (SiO_3)^{-2}$.

C. Mica type, SiO_4 tetrahedra forming sheets of indefinite extent, their formula $\infty\ (Si_2O_5)^{-2}$.

D. Feldspar type, SiO_4 tetrahedra united to form extended net-works, their formula $\infty\ (Si,Al)O_2$, (SiO_2 type).

Machatschki's classification is based, like those of his predecessors, primarily upon the number of combining SiO_4 tetrahedra, whether finite or infinite, and secondarily, upon the geometric forms of the resulting structures.

(e) In 1936 *C. Hermann, O. Lohrmann, H. Philipp*, adopted a classification[29] that is essentially that of W. L. Bragg, save that they divide his first group, with separate SiO_4 tetrahedra, into two parts. Their divisions are as follows:

I. Separate SiO_4 tetrahera, with other anions.
II. Separate SiO_4 tetrahedra, without other anions.
III. Finite groups of SiO_4 tetrahedra forming open groups or rings.
IV. One-dimensional infinite Si-O chains.
V. Two-dimensional extended Si-O nets.
VI. Three-dimensional extended (Si, Al)-O lattices.

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[27] Náray-Szabö, St. v., *Zeits. Phys. Chem.*, Ab. B, Bd. 9, pp. 356–377, **1930.**

[28] Machatschki, F., *Geol. Förenigens I, Stockholm Förhandlinger*, Bd. **54,** pp. 447–470, 1932.

[29] Hermann, C., Lohrmann, O., Philipp, H., *Zeits. Krist.*, Ergänzungsband, *Strukturbericht*, II, p. 20, **1936.**

2. Classification Proposed

The classification proposed by the author has many features in common with those of others. It differs from them, however, in the following respects:

(a) It is based upon the manner in which the SiO_4 tetrahedra combine and not upon the geometric forms of the structures resulting. We believe that the former is the cause of the latter. We hence regard it as more fundamental.

(b) It is based upon one simple, progressive method. There is no known simple method for predicting all the possible geometric forms of the structures. It is believed to be simpler.

(c) It is true chemically. All members of one fundamental type have the same general chemical formula; all bodies of the same general formula are placed in the same fundamental type. These statements are not true of the other suggested groupings.

(d) The complex types of silicates are distinguished, and their relations to those of simpler types are shown. The complex silicates which have very different structures have been placed in earlier classifications, without discrimination, in simpler types. The subject is more complex than has hitherto been recognized.

SUMMARY

The fundamental fact in the classification of the natural silicates is the combination of the SiO_4 tetrahedra by their solid angles. Five fundamental types are developed upon this basis and described. It is shown that the fundamental types may combine further to form complex types whose characteristics are considered. The relations of this classification to earlier classifications is discussed.

In the second part, to be published later, the composition and classification of the species of natural silicates will be given as far as they have been determined by x-ray investigation, with references to the literature in which their structures are described.

The following table gives the composition of the families of the natural silicates thus classified, as far as their structures have been determined by x-ray investigation.

FAMILIES OF SILICATES

SiO_4 tetrahedra united by		I ORTHOSILICATES R_4SiO_4 0 angles. Separate	II ORTHODISILICATES $R_6Si_2O_7$ 1 angle. Pairs		III METASILICATES R_2SiO_3 2 angles. Rings and Chains	IV METADISILICATES $R_2Si_2O_5$ 3 angles. Sheets	V DIOXIDE TYPE SiO_2 4 angles. Net-works
BIVALENT	ANHYDROUS	Olivine fam. $(Mg,Fe)_2SiO_4$ Phenacite fam. $(Be,Zn)_2SiO_4$	R'' Melilites $Ca_2(Mg,Zn)Si_2O_7$	Rings Chains	Wollastonite fam. $R''SiO_3$ $R''=(Ca,Mn)$ R'' Pyroxenes $R''_2Si_2O_6$ $R''=(Ca,Mg,Fe)$		
	HYDROUS-F	Chondrodite fam. $nMg_2SiO_4 + Mg(OH,F)_2$ *C. Bertrandite* $Be_2(BeOH)_2\left/\begin{matrix}SiO_4\\SiO_3\end{matrix}\right.$ I-III	Calamine $Zn_4(OH)_2Si_2O_7H_2O$	Chains	*R'' Amphiboles* $R''_7\left/\begin{matrix}Si_4O_{12}\\Si_4O_{10}\end{matrix}\right/(OH,F)_2$ $R''=(Ca,Mg,Fe)$ III-IV *C. Chrysotile* $(MgOH)_6\left/\begin{matrix}(Si_2O_6)\\(Si_2O_5)\end{matrix}\right/+H_2O$ III-IV	Apophyllite $4CaSi_2O_5KF.8H_2O$ Talc $Mg_3Si_4O_{10}(OH)_2$	
TRIVALENT	ANHYDROUS	Garnet fam. $R''_3R'''_2(SiO_4)_3$ Cyanite Group Al_2OSiO_4 Eulytite fam. $Bi_4(SiO_4)_3$	R''' Melilites $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$ Thortveitite $Sc_2Si_2O_7$	Chains Rings	R''' Pyroxenes $(X,Y)_2(Si,Al)_2O_6$ $X=(Ca,Na,K)$ $Y=(Mg,Fe,Al,Mn,Ti,Li)$ Beryl $Be_3Al_2(SiO_3)_6$ Cordierite $Mg_2Al_3Si_5AlO_{18}$		Nepheline $(Na,K)AlSiO_4$ Leucite* $KAlSi_2O_6$ Feldspar fam. $R_{1-2}(Al,Si)_4O_8$ Danburite $CaB_2Si_2O_8$ Scapolite fam. $\left\{\begin{matrix}3Ab+NaCl\\3An+Ca(CO_3,SO_4)\end{matrix}\right.$ Sodalite f. $(Na,Ca)_{6-3}(SiAlO_4)_6\left\{\begin{matrix}Na_2Cl_2\\Na_2SO_4\\(CaSO_4)_{1-2}\end{matrix}\right.$ Cancrinite fam. $3Ne+Ca(Cl_2,CO_3,SO_4)$ Helvite f. $3(Mn,Fe,Zn)(Be,Si)_2O_4(Mn,Fe,Zn)S$
	HYDROUS-F	Staurolite 2 Cyanite + $Fe(OH)_2$ Topaz $Al_2(OH,F)_2SiO_4$ Euclase $AlBeOHSiO_4$ *C. Vesuvianite* $Ca_{10}Al_4\left/\begin{matrix}(SiO_4)_5\\(Si_2O_7)_2\end{matrix}\right/2Mg(OH)_2$ I-II	Meliphanite fam.* $(Ca,Na)_2Be(Si,Al)_2(O,OH,F)_7$ *C. Zunyite* $Al_{12}\left/\begin{matrix}(Si_2O_7)_2\\SiO_2\\AlO_4\end{matrix}\right/(OH,F)_{18}Cl$ II-V	Chains	*C. R''' Amphiboles* $X_{2-3}Y_5\left/\begin{matrix}(Si,Al)_4O_{12}\\(Si,Al)_4O_{10}\end{matrix}\right/(OH,F)_2$ $X=(Ca,Na,K)$ $Y=(Mg,Fe,Al,Mn,Ti,Li)$ III-IV	Kaolin fam. $Al_2Si_2O_5(OH)_4$ Pyrophyllite $Al_2Si_4O_{10}(OH)_2$ Montmorillonite $(Mg,Al,Fe)_{2-3}(Si,Al,Fe)_4O_{10}(OH)_2nH_2O$ Micas $R_{7-8}(Si,Al)_4O_{10}(OH)_2$ Vermiculites $(Mg,Fe)_{2-3}(Si,Al,Fe)_4O_{10}(OH)_2 4H_2O$ Chlorites $R_{13-14}(Si,Al)_4O_{10}(OH)_8$ *C. Epididymite* $NaBeOH\left/\begin{matrix}Si_2O_5\\SiO_2\end{matrix}\right.$ IV-V	Zeolites $R_mAl_mSi_nO_{2(m+n)} \times H_2O$ $R=Ca,Na,Ba,Sr,K$
QUADRIV.	ANHYDROUS	Zircon fam. $(Zr,Th)SiO_4$ Titanite fam. $Ca(TiO)SiO_4$	R				

THE OPTIC PROPERTIES OF SEIGNETTE AND RELATED SALTS

A. N. WINCHELL, *University of Wisconsin, Madison, Wisconsin.*

For more than a century the optic properties of Seignette salts have attracted attention; but, nevertheless, they are still imperfectly known. Herschell[1] described the strong dispersion of sodium-potassium tartrate tetrahydrate (Seignette or Rochelle salt) as early as 1829. Senarmont[2] studied the properties of the ammonium-potassium series of tartrates in 1851. Des Cloizeaux[3] measured the optic angle and refractive indices of Seignette salt in red and yellow light in 1858. Muttrich[4] made similar measures in red light at 16° and 45°C in 1864. Wyrouboff[5] measured ammonium Seignette salt in 1884. Lavenir[6] repeated these measures on potassium Seignette salt in sodium light in 1894. Bacuvier[7] repeated such measures on both potassium and ammonium Seignette salts and also on seven different proportions of mix-crystals in 1922. Buckley[8] studied the dispersion of Seignette and related salts in many kinds of pure and mix-crystals. Recently, Kozik[9] has studied the optic properties of sodium-rubidium tartrate and also of mix crystals of sodium-ammonium and sodium-rubidium tartrates.

In view of all these studies it is fair to ask why the subject should be investigated farther. The answer is that previous investigators have made no attempts to correlate their results, particularly in the form of graphs. Such correlations bring out certain imperfections in the data and lead to conclusions of interest.

The series from sodium-potassium tartrate (Seignette salt proper or potash Seignette salt) to sodium-ammonium tartrate (ammonium Seignette salt) has been studied most fully in the past. Published data showing the relations between optic properties and composition are assembled in Fig. 1. The indices of refraction as measured by Bacuvier require optic angles as follows, as compared with the measured optic angles:

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[1] *Edinburgh Jour. Sci.*, vol. **10,** p. 296, 1829.

[2] *Ann. Chem. Phys.*, vol. **33,** pp. 416, 429, 1851.

[3] *Ann. Mines*, vol. **11,** p. 321, 1857; vol. **14,** p. 367, 1858.
Also Seve, *Jour. Phys.*, Series VI, vol. **I,** p. 176, 1920.

[4] *Ann. Phys.*, vol. **121,** p. 193, 1864.

[5] *Bull. Soc. Fr. Min.*, vol. **7,** p. 8, 1884.

[6] *Bull. Soc. Fr. Min.*, vol. **17,** p. 153, 1894.

[7] *Bull. Soc. Fr. Min.*, vol. **45,** p. 73, 1922.

[8] *Mineral. Mag.*, vol. **20,** p. 159, 1924; and vol. **21,** p. 55, 1926.

[9] *Bull. Int. Acad. Polon. Sci. Varsovie.* A., p. 229, **1927,** and p. 247, **1931.**

%NH₄	17	27	30	36	52	72	76
%K	83	73	70	64	48	28	24
2*V* over *X* (calc.)	86°	84°	93°	87°	84°	72°	76°
2*V* over *X* (meas.)	64°	50° 40′	44° 25′	5°	40°	48°	50° 40′

The diagram indicates that the measurements of the optic angle are much more accurate than the measurements of the indices.

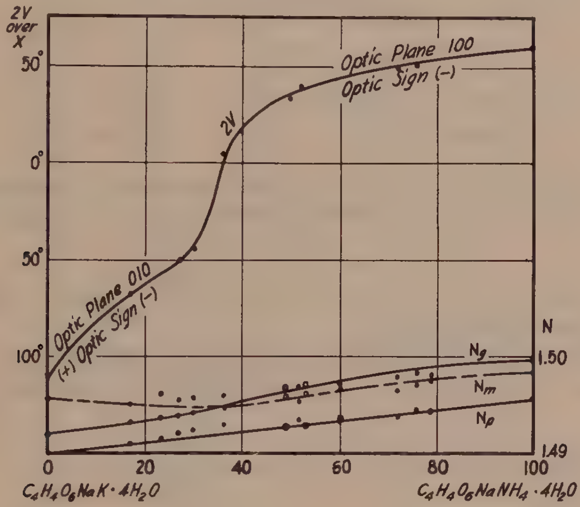

FIG. 1. Variations of optic properties for λ = 589 in Seignette salts. Data of L. Bacuvier: (•) *Bull. Soc. Fr. Min.*, vol. **45**, p. 73, 1922; and H. E. Buckley: *Mineral. Mag.*, vol. **20**, p. 159, 1924, and vol. **21**, p. 55, 1926; and A. Lavenir: (°) *Bull. Soc. Fr. Min.*, vol. **17**, p. 153, 1894.

The indices of refraction as measured by Lavenir require optic angles as follows as compared with the optic angles derived from the diagram (Fig. 1):

%NH₄	23	47	53	60	79
%K	77	53	47	40	21
2*V* over *X* (calc.)	86°	67°	38°	46°	27°
2*V* over *X* (diagram)	57°	33°	40°	45°	53°

Two of these check very well, but the others do not, although the measures of N_p seem to be exceptionally accurate.

The optic angle has been measured by Buckley in three intermediate types of the series from sodium-ammonium tartrate to potassium-ammonium tartrate; the simple variation in the series is shown in Fig. 2.

In the series from potassium-ammonium tartrate to sodium-potassium tartrate (also measured by Buckley) the variations in the optic angle are much greater; the optic angle varies through 0° (with change in the position of the optic plane) and also through 90° (with change in the optic sign), as shown in Fig. 3.

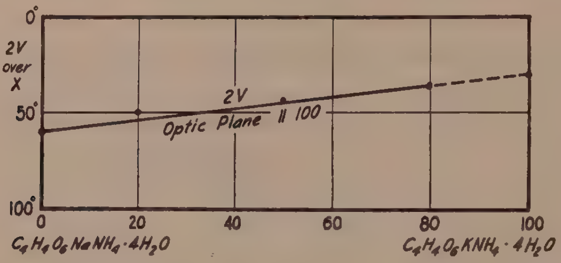

FIG. 2. Variations of optic angle for λ = 578 in sodium-ammonium to potassium-ammonium tartrates. Data of H. E. Buckley: *Mineral. Mag.*, vol. **21**, p. 55, 1926.

Variations in the optic sign, optic angle, and position of the optic plane in the entire ternary system, NaK-$NaNH_4$-KNH_4 tartrates, are shown in Fig. 4. This diagram is based entirely on the three binary series; no data are available for points inside of the triangle.

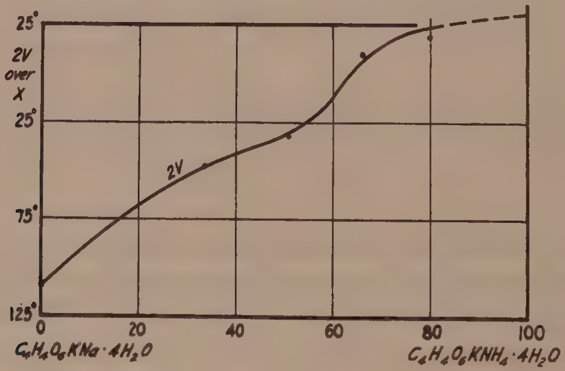

FIG. 3. Variations of optic angle for λ = 578 in potassium-sodium to potassium-ammonium tartrates. Data of H. E. Buckley: *Mineral. Mag.*, vol. **21**, p. 55, 1926.

Buckley also shows that $NaNH_4$ and Na_2 tartrates form a series, the variation of the optic angle in which is shown in Fig. 5.

In a similar series from $NaNH_4$ to $(NH_4)_2$ the optic angle varies as shown in Fig. 6.

Kozik has studied the series of tartrates from sodium-ammonium to sodium-rubidium; he measured the optic angle and also the refractive indices of the pure salt and also of four intermediate types. His results are shown graphically in Fig. 7, which is consistent with the work of others except for the measures for N_p, which cause an unexplained break in that curve.

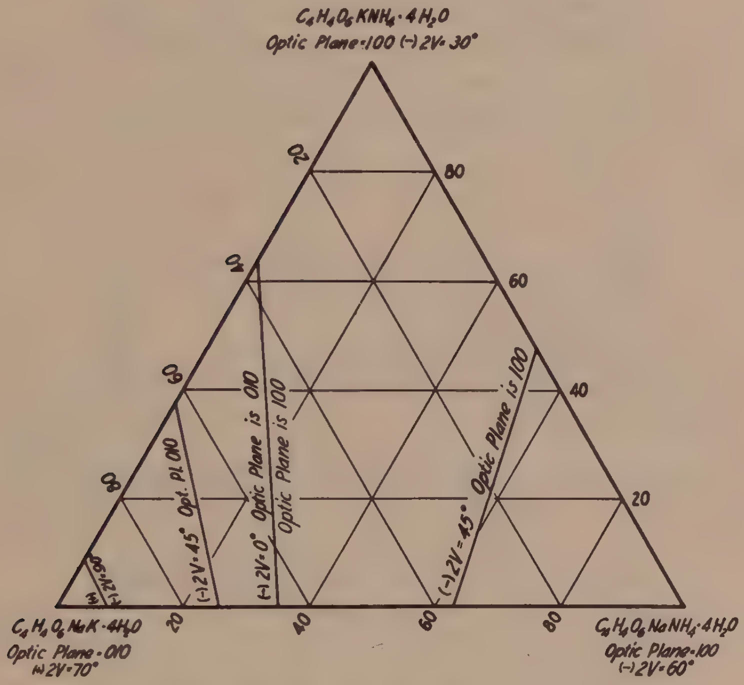

FIG. 4. Variations of optic angle, sign, and optic plane for λ=578 in the $KNH_4-NaK-NaNH_4$ system of tartrates. Data of H. E. Buckley: *Mineral. Mag.* vol. 21, p. 55, 1926.

The data of Kozik on the NaRb to $NaNH_4$ series permit the preparation of sketch of the entire NaRb-$NaNH_4$-NaK ternary system, shown in Fig. 8. Data for the NaRb-NaK series and also for all points inside the triangle are not available, but the differences between this ternary system and the one shown in Fig. 4 are very distinct.

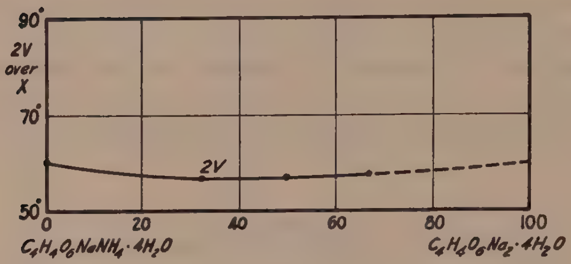

FIG. 5. Optic angle for λ=578 in sodium to sodium-ammonium series of tartrates. Data of H. E. Buckley: *Mineral. Mag.*, vol. **21**, p. 55, 1926.

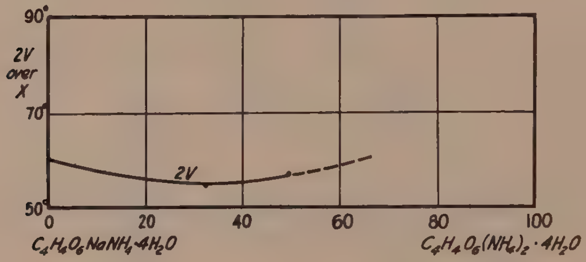

FIG. 6. Optic angle for λ=578 in ammonium to sodium-ammonium series of tartrates. Data of H. E. Buckley: *Mineral. Mag.*, vol. **21**, p. 55, 1926.

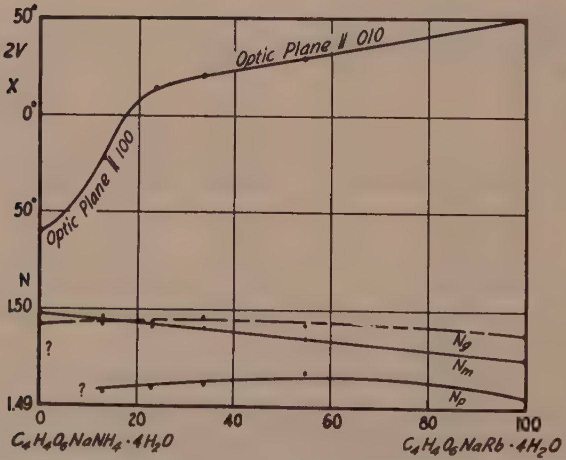

FIG. 7. Variations in the optic properties in sodium light in sodium-ammonium to sodium-rubidium tartrate. Data S. Kozik: *Bull. Int. Acad. Polon. Sci. Lit., A*, p. 229, **1927**, and p. 247, **1931**.

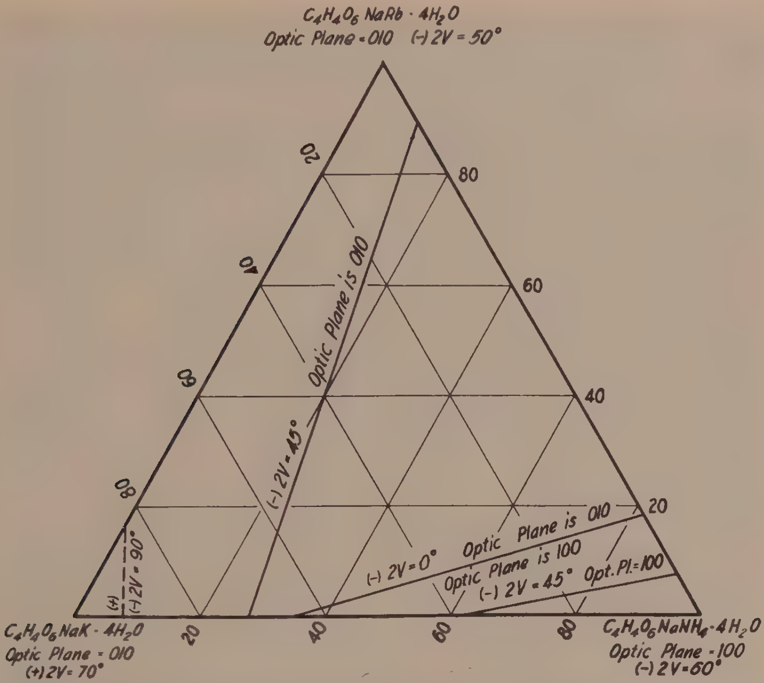

Fig. 8. Variations of optic angle, sign, and optic plane in the NaK—$NaNH_4$—NaRb system of tartrates. Data of H. C. Buckley: *Mineral. Mag.*, vol. **21**, p. 55, **1926**, and S. Kozik: *Bull. Int. Acad. Polon. Sci. Lit. I, A*, p. 247, **1931**.

MEMORIAL OF ALEXANDER HAMILTON PHILLIPS

A. F. BUDDINGTON, *Princeton University,*
Princeton, New Jersey.

Professor Alexander Hamilton Phillips died at his home in Princeton, New Jersey, January 20, 1937, at the age of seventy years. Professor Phillips was a warm friend of all mineralogists, from the boy collector with his first specimens to the professional research scientist. He had both a real love for minerals as specimens and a deep interest in them as subjects for scientific research.

He was born and grew up on the family farm near Lawrenceville, New Jersey, only a few miles from Princeton. He was the son of John Feaster and Hannah Warne Phillips. He married Miss Mabel Harriet Knight of New York City in 1896. Mrs. Phillips died in 1934. They had no children.

Professor Phillips entered Princeton University in 1883 and graduated with the degree of B.S. in the class of 1887. He continued his studies while teaching at the University after graduation, and received the Sc.D. in 1899. As an undergraduate he took a very large number of courses (37 semester courses) in science and mathematics, and was elected to Phi Beta Kappa in his senior year. His courses in science were mostly in biology, chemistry, and mineralogy. In the early period of his active services, the present diversification and specialization in science were not so marked, and one could be competent in several fields. This is well exemplified in Professor Phillips' career.

For a period of 49 years following his graduation from Princeton in 1887, Professor Phillips was an official member of the staff of instruction at Princeton. He had the unique distinction of serving successively in three departments. The breadth of his experience can best be indicated by citing the courses he taught. For six years he was a member of the Biology Department, assisting in such courses as Vertebrate Morphology; Comparative Anatomy and Embryology; and Morphology of Birds and Reptiles. During this time he was associated with Professors W. B. Scott, and H. F. Osborn, and was for two years under his brother John Warne Phillips (Demonstrator in Biology). The following 13 years, with the exception of one year, he was a member of the Department of Applied Chemistry and Mineralogy, and taught courses in Qualitative Analysis; Quantitative Analysis, whose content was described as "including salts, limestone, coal, feldspar, etc., and sugars, milk and similar food analyses"; Advanced Quantitative Analysis including complex substances, such as iron, steel, etc.; Assaying; and Blowpipe Analysis. For one year (1903–1904) he was a member of a separate department of Mineralogy

ALEXANDER HAMILTON PHILLIPS
(1866–1937)

together with Professor Cornwall. From 1905 to 1936 he was a member of the Department of Geology and taught courses in Blowpipe Analysis, Descriptive Mineralogy, Optical Mineralogy and Crystallography, Petrography, and Advanced Mineralogy, including crystallography and the paragenesis and chemical relations of minerals.

Professor Phillips was recognized by all those who had occasion to come in contact with his work as a thoroughly competent chemical analyst, and his main research activities were largely directed at problems which involved chemical analysis. His first published paper (1894) was based on two chemical analyses of rock from Hawaii; his doctorate dissertation (1899) was a thoroughgoing microscopic and chemical study of the trap rock of Rocky Hill, New Jersey. This contained nine complete chemical analyses comprising three specimens of rock from three different vertical positions in the sill, and chemical analyses of two augites and four plagioclases from the analyzed rock specimens. The difference in composition of the augites and of the plagioclases was explained in terms of fractional crystallization, an early recognition of this important principle in interpreting certain mineral and rock relationships. At the time of his death he had completed a series of 30 chemical analyses of minerals and rocks for a series of papers in which he was collaborating with Dr. H. H. Hess, and had finished all the weighings of precipitates and volumetric determinations for another analysis, but had not made any of the calculations to determine the oxides. The writer made the appropriate computations and the total added up to 99.91 per cent, a result quite in keeping with his uniform accuracy.

In 1904 he published a paper on "Radium in an American Ore." This presented the preliminary basis for a method of concentrating radium from Colorado carnotite (hydrous potassium uranium vanadate), a process founded largely on the principle of fractional crystallization. The concluding sentence of his paper was "These facts prove beyond question that carnotite will become a commercial source of radium." Radium was first produced on a commercial scale from this ore in this country in 1914.

In 1914 Professor Phillips undertook an analytical search for metals in marine organisms from the Tortugas, collected in collaboration with his colleague, Professor van Ingen. Since the amount of metallic constituents ranged from only a few ten thousandths to a few hundredths of a per cent, the task was an exceedingly delicate one. Minute amounts of copper, iron, zinc, and manganese were found in all the materials examined, as well as lead in the liver of a horse conch, and vanadium to the extent of 0.12 per cent in a dried holothurian. These results were of importance in connection with the possible role of organisms as a source of the minor metallic constituents of sedimentary rocks.

He aided materially the researches of his colleagues and of graduate students through advice on chemical problems and through the contribution of a great many chemical analyses.

His analytical studies also led him to the discovery and description of a new mineral (gageite) from Franklin Furnace. He also discovered some new zinc phosphates from Salmo, B. C., but was anticipated in publication by Dr. T. L. Walker of Toronto.

Aside from the chemical studies, he published several papers describing new crystallographic forms for minerals, and his presidential address before the Mineralogical Society in 1931 was on "Isomorphous substitution of elements in minerals."

Professor Phillips was the author of a comprehensive textbook of mineralogy, which included tables for determining all but the very rare minerals by means of the blowpipe. This latter subject was one of his special interests.

He had the ingenuity of the traditional Yankee. All of the highly complicated crystal models, of which he had a magnificent collection he made himself from the wood of a pear tree grown in his own back yard. He also made a set for Mt. Holyoke College when fire destroyed their collection.

Professor Phillips was very active in university affairs and served on many of the major committees of administration where, in the words of Dean L. P. Eisenhart, "his fine spirit, deep human sympathy, and sound judgment were of great value."

He was an ardent fisherman and also an amateur ornithologist. His interest in wild life, combined with his broad scientific background, enabled him to render valuable services to the State of New Jersey as a member of the State Fish and Game Commission from 1919 to the date of his death. In this capacity he has had virtual direction of the Hackettstown Fish Hatchery, with the result that pioneering work was done in many fields and the hatchery is now one of the foremost in the country. His services were much in demand as a toastmaster and speaker at dinners of sportsmen.

Professor Phillips was one of a rather small group that was vitally interested in the organization of the Mineralogical Society of America, and was chairman of the organization committee (December 1919) and one of the Charter Fellows of the Society. He served the Society as Councilor (1920–1923), Treasurer (1924–1929), and President (1931), and was always influential in the affairs of the Society.

He was a Fellow of the Geological Society of America (1914–1937) and Vice President for the year 1931; also Fellow of the American Association for the Advancement of Science, the Society of Naturalists, and the American Chemical Society.

Professor Phillips served his community in many official positions and capacities. He was a member of the Borough Council from 1906 until 1911, and Mayor of Princeton from 1911 until 1916. During the World War he was food administrator of the Borough. For the last year of his life he served as Recorder of the Borough and was held in deep respect by those in all walks of life for his humane, fair, and impartial administration of justice.

For nearly 32 years Professor Phillips' interests centered in the Department of Geology at Princeton, and by his will he provided a substantial fund for the furtherance of the work of that department and for additions to its mineralogical collections.

Professor Phillips was a scholar of varied interests, broad experience, and excellent judgment. He was noted far and wide for his deep laugh, and his good humor and congeniality were contagious. The interests of the Mineralogical Society of America were close to his heart, and the members of the Society accorded him a deep fondness, admiration, and respect. We mourn the loss of a very great personality.

RIEBECKITE IN QUARTZ VEINS FROM THE MICHIPICOTEN DISTRICT, ONTARIO

J. E. Hawley, *Queen's University, Kingston, Ontario.*

Abstract

A fibrous variety of riebeckite is described as occurring in quartz veins and in both granitic and basic volcanic wall rocks in the Michipicoten area, Ontario. It represents one of the last stages of hydrothermal alteration, replacing all other minerals present, but particularly quartz, greenish muscovite, epidote and carbonates. As gold in nearby veins is also described as one of the last minerals to be deposited in the veins the question is raised as to a genetic relationship existing between it and the riebeckite.

The occurrence of fibrous riebeckite in quartz veins and in adjacent wall rocks in the Michipicoten area, Ontario, is sufficiently rare to merit a brief description. Its development in the quartz and replacement of biotite and epidote in adjoining rocks throw additional light on the nature of the hydrothermal solutions accompanying vein formation.

Specimens of riebeckite in quartz vein matter with granitic wall rock attached were collected by Mr. O. A. Evans of Sault Ste. Marie in 1933, from the vicinity of the Parkhill and Minto Gold Mines and were forwarded to the writer for identification. A. G. Darling studied the mineral for a bachelor's thesis. Dr. E. L. Bruce kindly made a spectrographic analysis of the mineral.

Previous Work in Michipicoten Area

The general geology of the Michipicoten area is described by T. L. Gledhill.[1] M. H. Frohberg[2] has written in detail regarding the quartz-tourmaline, gold-bearing veins of the same district, and discusses the metamorphism attending their introduction, but no mention is made by either of the above authors of riebeckite as a constituent of the veins or containing rocks. Its occurrence even in this area would appear, therefore, to be rare.

Gledhill relates the quartz veins to an Algoman series grading from diorite to granodiorite and quartz porphyry, which intrude schistose, basic, Keewatin lavas. The veins are classified as fissure fillings varying somewhat in their mineral content. They follow the contacts between intrusives and lavas but also cut across both. Gledhill infers a two-stage mineralization, the first characterized by introduction of quartz, sulphides including chalcopyrite, pyrrhotite, pyrite, galena, sphalerite, and arsenopyrite, and probably some gold, solutions accompanying which are believed to have produced various wall rock alterations, the second consisting chiefly of the introduction of gold along fractures in the earlier sulphides.

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[1] Gledhill, T. L., Michipicoten gold area, District of Algoma: *Ann. Rept. Ont. Dept. Mines*, vol. **36**, Pt. II, 1927.

[2] Frohberg, M. H., Beiträge zur Kenntnis der turmalin führenden-gold-quarz gänge des Michipicoten-Distriktes, Ontario: *Min., petrogr. Mitt.*, **44**(5), pp. 349–409.

PROPERTIES OF MICHIPICOTEN RIEBECKITE

Physical. It occurs in botryoidal, reniform and globular aggregates composed of columnar, radiating, or felt-like masses of fibers, .01 mm. in diameter or less. Lacks asbestiform habit.

Optical. $N_g = 1.699$
$N_m = \ ?$
$N_p = 1.693$
$2V =$ large
Sign: +, as obtained from parallel groups of fibers, angle of rotation of bisectrix figure over 30°.
Color: dark blue, pleochroic with absorption, X much stronger than Y and Z
$X =$ deep blue in thick aggregates, light greenish blue in thin fibers.
$Y =$ light yellowish green.
$Z =$ deep blue, thick; gray, thin.
Interference color: ultra or Berlin blue.
$X \wedge c = 0° - 5°$
Dispersion: strong.

Extinction angles measured with fibers in position of least absorption give the following:

$$X \wedge c = (600\ \mu\mu)\ 5\tfrac{1}{2}°$$
$$= (589\ \mu\mu)\ 7°$$
$$= (550\ \mu\mu)\ 9°$$

Chemical. A spectrographic analysis of the mineral shows the presence chiefly of iron, silicon and sodium. For comparative purposes plates were made of asbestiform South African crocidolite and the Michipicoten mineral; identical spectra were obtained. Two samples of the Michipicoten mineral were analyzed by A. G. Darling for sodium according to the method recommended in Fales "Inorganic Quantitative Analysis." The average sodium obtained in the two 0.1 gram samples was 4.80 per cent ($Na_2O = 6.47\%$). This compares well with the calculated 4.92% sodium, using Winchell's formula for riebeckite as $H_2Na_2Fe_5Si_8O_{24}$, and also with analyses of South African and other crocidolites given in Dana's "System of Mineralogy"[3] as ranging from 5.69 to 7.71 per cent Na_2O. It is somewhat lower in soda than analyses of riebeckite which vary from 8.33 to 8.79 per cent Na_2O.

Alteration. Where oxidized the mineral turns brown and the birefringence increases considerably.

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[3] Dana's *System of Mineralogy*, p. 400.

IDENTIFICATION

On the basis of extinction angles, sign, and chemical similarity to crocidolite, the Michipicoten mineral is classified as a variety of riebeckite. Unfortunately no analyses of ferrous and ferric iron are available at present to further distinguish it from arfvedsonite.

Though possessing a fibrous habit and probable positive sign the mineral is not here classified as the variety crocidolite because of lack of asbestiform habit.

OCCURRENCE

In the Michipicotin area, deep blue riebeckite is found in a few quartz veins and in both granitic intrusives and basic Keewatin volcanics near the veins.

Occurrence in Veins

Within the veins it is confined to areas near the walls, filling or partly filling vugs and following fractures in greasy, gray quartz in irregular seams up to $\frac{1}{4}$ inch in width. In one specimen fine pyrite is associated with the riebeckite.

In thin section the riebeckite occurs chiefly as small globular bodies .05 to .5 mm. in diameter, irregularly replacing the quartz, and from the globules fine fibers project outward. One section shows the riebeckite filling fractures in broken pyrite grains, so it is definitely later in age than both quartz and pyrite.

The globular forms assumed by the riebeckite suggest a gel origin with subsequent crystallization.

Occurrence in Wall Rocks

Wall rocks containing the riebeckite which have been examined microscopically consist only of a granitic type and of a carbonate-brown biotite alteration zone.

In the former, medium grained feldspars consist now of albite, probably secondary after oligoclase. Quartz, biotite, and apatite are the other primary minerals. Secondary flakes of a greenish muscovite, clinozoisite and epidote replace the feldspars, quartz, and biotite, as also does riebeckite. The latter is developed particularly in aggregates of the light green mica and epidote, and definitely cuts both biotite and epidote. Replacement of the green muscovite is clear, and probably also of epidote. This appears in both cases to be gradual, the minerals becoming more strongly pleochroic in yellow and greenish blue but retaining a relatively high birefringence. Where the replacement is more complete the pleochroism becomes that of riebeckite and interference colors are gradually lowered to an ultra blue.

In the carbonate-biotite alteration product riebeckite is again found replacing greenish muscovite, transecting flakes of brown biotite, and replacing the carbonates, particularly along cleavages. It would appear, therefore, that the riebeckite is one of the latest minerals to develop in both the veins and wall rocks.

Hydrothermal Alterations Associated with Michipicoten Veins

The hydrothermal metamorphism of the wall rocks of the gold-bearing quartz veins of the Michipicoten area according to Gledhill[4] consists of two types. The more basic rocks (lavas) show the development near the veins and lamprophyre dykes of biotite and a "bluish green chlorite" (*riebeckite?*). The granodiorite intrusive at the Minto mine is altered near the veins to biotite, carbonates, sericite and quartz. Tourmaline is developed both in vugs in the quartz and in sheared walls. Analyses presented show a relative introduction of silica, alumina, potash and carbon dioxide, and a loss particularly of soda and lime.

Frohberg[5] on the other hand classifies the metamorphism as progressive and denoted by three important stages. The earliest alteration is the development of albite and biotite, the former particularly in plagioclase rich rocks. Tourmaline is a common associate, also clinozoisite, and arsenopyrite is noted as the chief early sulphide. Chemically this stage involves an addition of soda, alumina, and magnesia, and a loss of potash, lime, and silica. Second is the alteration of biotite to chlorite, the serpentinization of epidote, and the introduction of minor carbonates. The last stage is marked by the formation of sericite and carbonates in albite, chorite, biotite, and serpentine. Chemically as shown previously by Gledhill, soda is lost together with lime in this stage and potash is gained relatively. A still later development of carbonates locally replaces sericite, tourmaline and many sulphides.

While the present study has been limited by the few specimens available, it has been sufficient to indicate essential agreement with the successive stages of hydrothermal alteration outlined by Frohberg, but to his list there remains to be added the final development of riebeckite which is distinctly later than pyrite, biotite, epidote, muscovite and carbonates. Chemically its formation has involved essentially a second introduction of soda. In the pseudomorphous replacement of muscovite, which is most common, soda would presumably displace the potash, and iron, the alumina. A somewhat similar conversion of epidote to riebeckite is suggested in thin sections but because of the fine size of the former its identity is not certain. Such a change might involve the substitution of soda for lime, though no sodium bearing epidotes appear to have been described.

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[4] *Op. cit.*, p. 23.

[5] *Op. cit.*

Since Gledhill[6] has called attention to the fact that some of the gold of the veins has been introduced "by alkaline solutions . . . after the sulphides were fractured," that is, as one of the last minerals, the question may logically be raised as to whether or not these final auriferous solutions were rich in soda, and as well as precipitating gold gave rise to the formation of riebeckite. In this connection attention may be called to Freeman's[7] suggestions that sulphides of many of the metals may be transported in part as double sodium sulphides which break down to colloidal sulphides (or free gold where it is present) in contact with water. While the sodium in solutions resulting from such decomposition might be completely removed in many cases because of its great solubility, the formation of sodium-rich minerals such as riebeckite might be a logical result in others. The globular form of the riebeckite would be in keeping with such an hypothesis, suggesting as it does an original colloidal origin.

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[6] *Op. cit.*, p. 29.

[7] Freeman, Horace, *Eng. Min. Journ. Press*, Dec. 19, 1925.

SELECTIVE INCRUSTATION OF MINERALS

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Introduction

In the sequential deposition of minerals in an open space, a tendency may be observed for a species of later formation to crystallize by preference upon the drusy crystals of one of the earlier formed species only, instead of indiscriminately incrusting all of the species present.

Such a tendency has been recognized by Miers,[1] who called attention to:

> . . . the tendency exhibited by a given mineral to crystallize only upon certain minerals, and not upon others . . . The reluctance of quartz to crystallize upon the metallic minerals is strikingly conspicuous. A survey of any mineral collection brings this fact to light at once.

The same tendency was noted by Smyth,[2] in describing an occurrence of pyrrhotite with dolomite, calcite and quartz in limestone from Lairdsville, N. Y. Smyth stated that:

> The placing of the pyrrhotite with reference to the other minerals affords a very pretty example of selective precipitation . . . When a cavity contains calcite with quartz and dolomite, the pyrrhotite is deposited upon this mineral almost exclusively . . . When calcite is lacking in a cavity dolomite supports the pyrrhotite and it is only when the crystals of this mineral become large and very abundant that they rest upon quartz.

Cross and Hillebrand[3] noted that aragonite occurs as an incrusting mineral associated with zeolites in cavities in the basalt of North Table

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[1] Miers, H. A., *Mineral., Mag.*, vol. **11,** p. 275, 1897.

[2] Smyth, C. H., *Am. Jour. Sci.*, ser. 4, vol. **32,** pp. 156–160, 1911.

[3] Cross, C. W., and Hillebrand, W. F., *U. S. Geol. Survey, Bull.* **20,** p. 39, 1885.

Mountain, Colorado, and comment that it apparently has a special tendency for deposition upon chabazite. Elsewhere these authors stated that the thomsonite at this locality seems specially suited to attract the deposition of mesolite.[4] Mügge[5] has cited several instances in which chalcopyrite has incrusted tetrahedrite in preference to quartz and other minerals. Photographs have been published by Boutwell[6] of specimens apparently exhibiting incrustations of tetrahedrite upon chalcopyrite in preference to pyrite, and of sphalerite incrusting tetrahedrite in preference to quartz, but the specimens are not specifically described in the text of the papers.

On the following pages, a number of additional instances of selective incrustation are described, and the origin of the selectivity is discussed. Most of the specimens described are contained in the collections of the American Museum of Natural History, Columbia University and Harvard University. In addition, a few instances are described from the collection of the Philadelphia Academy of Natural Sciences, and from other sources. Approximately 40,000 specimens were examined for selectivity in the course of the survey.

Acknowledgments. The writer wishes to express his thanks to Mr. Herbert P. Whitlock, Prof. Paul F. Kerr, Dr. Harry Berman and Mr. Samuel G. Gordon for a discussion of the paragenetic relations on a number of the specimens, and to Prof. E. A. Hauser, Massachusetts Institute of Technology, for a discussion of certain aspects of colloid chemistry relevant to the problem.

ADSORPTION CONTROL OF MINERAL INCRUSTATION

As is well known, the surface of a crystal possesses a degree of residual affinity, and can attract and hold—adsorb—atoms, ions and molecules. The crystallization of a substance from solution upon the surface of a crystal immersed in the solution is, in general, influenced by the adsorption at that surface.

Kinds of Mineral Incrustations. Several different kinds of mineral incrustations, illustrative of adsorption control of super-crystallization, can be recognized. With single crystals presenting several forms, the crystallization of an incrusting mineral may be favored upon the faces of one of the crystal forms to the exclusion of the others, as a consequence of the stronger adsorptive power of that form.[7]

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[4] Cross, C. W., and Hillebrand, W. F., *Am. Jour. Sci.*, ser. 3, vol. **23**, p. 246, 1882; ser. 3, vol. **24**, p. 133, 1882.

[5] Mügge, O., *Neues Jahrb., Beil. Bd.* **16**, p. 361, 1903.

[6] Boutwell, J. M., *U. S. Geol. Survey, Prof. Paper* **38**, Pl. 38, fig. B, 1905; *U. S. Geol. Survey, Prof. Paper* **77**, Pl. 27, fig. B, 1912.

Similarly, the edges and corners of crystals, which are regions of greater adsorptive power than the adjacent plane faces, may be selectively incrusted.[8] Oriented incrustations are also effected by adsorption, the atoms of the adsorbed substance being regularly arranged upon the adsorbing surface and affording an ordered foundation layer for the overgrowing crystal.[9] Polar incrustations, in which hemimorphic crystals are attached to the matrix by a particular end of the polar axis,[10] as of hemimorphite, are also a consequence of adsorption control. Here the polar orientation of the crystal is imposed by the oriented, polar, adsorption of its asymmetric molecules at the surface before the start of crystallization.

Crystallization upon an adsorbing surface may also be marked by the appearance of abnormalities in habit development, distortion, twinning and other peculiarities absent in crystals of the same substance when grown suspended in the same solution.

Incrustations Selective Between Minerals. In the case of incrustations that are selective between minerals, the problem presented is that of a solution which is crystallizing in the presence of crystals of several different species, and upon the surface of one of which crystallization is favored to the exclusion of the others. Crystallization from solution tends to initiate upon a pre-formed surface present in the solution, rather than in the interior of the solution itself, partly because the concentration of the crystallizing substance may be greater there, because of adsorption, and partly because less free energy is required to form an attached crystal nucleus than a freely suspended nucleus of equal size.[7,9] If several different species of crystal surfaces are present in the solution, crystallization will be favored at the most strongly adsorbing surface. With the appearance of the initial nuclei, the super-saturation of the solution will be discharged, and deposition will tend to be confined to that particular species of surface, giving a selective incrustation.

Selective incrustations of this origin can be obtained by experiment. Sodium nitrate, for instance, is strongly adsorbed by calcite, and when crystallized from solution in the presence of fragments of calcite, quartz, aragonite, pyrite, etc., it deposits selectively upon the calcite. Similarly, the super-saturation necessary for the crystallization of sodium nitrate upon siderite, rhodochrosite and calcite varies, at a given temperature, with the crystal species.[11] Gypsum crystallizes more readily upon hydrophobic than upon hydrophilic surfaces.[12] The observation of Chevalier,[13] that particles of alum are most effective in inducing the crystallization of alum solutions, while particles of galena, spinel and fluorite are less effective, and particles of pyrite, cuprite and sphalerite are least effective, also constitutes a selective super-crystallization. Many similar observations could be cited.

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[7] Frondel, C., Selective incrustation of crystal forms: *Am. Mineral.*, vol. **19**, pp. 316–329, 1934. Some mineral incrustations selective upon crystal forms: *Am. Mus. Nat. Hist., Novit.*, no. **918**, pp. 1–4, 1937; no. **695**, pp. 1–6, 1934.

[8] Frondel, C., Mineral incrustations upon the edges and corners of crystals: *Am. Mus. Nat. Hist., Novit.*, no. **759**, pp. 1–11, 1934.

[9] Frondel, C., Oriented overgrowth and intergrowth in relation to . . . adsorption: *Am. Jour. Sci.*, ser. 5, vol. **30**, pp. 51–56, 1935.

[10] Holzner, J., *Zeits. Krist.*, vol. **65**, pp. 175–179, 1927; also ref. 7, p. 328.

Most of the observed instances of selectivity can be identified either with experimentally determined cases of strong adsorption, or satisfy the theoretical conditions for a strong adsorptive relation. In addition, a type of selectivity can be recognized in which the incrusting mineral appears to have been localized by chemical reaction (chemosorption) between the incrusted mineral and a solution or a colloidal dispersion. Incrustations formed by the superficial alteration of a mineral, such as crusts of anglesite upon galena, are excluded from the kind of incrustation considered here, in which super-deposition is the characterizing process. Nevertheless, no sharp distinction can be made between adsorption and chemical action, the crystal forces involved in both being identical.

Colloids and Mineral Incrustations. Adsorption by large crystals differs from adsorption by colloidal particles, largely in the nature of the effects produced. With crystals in the colloidal range of size, say from 1 to 500 μ, the effect of the adsorption may be to colloidally disperse them, or to produce other colloidal phenomena. With large crystals, on the other hand, the mass of the adsorbent is too great to permit dispersion, and the crystal, with its attached double layer, can be visualized as a massive, immobile micelle. Adsorption by crystals in this range of size may be manifested by the control exerted over super-crystallization; or, if the crystal is growing, by a modification of crystal habit, the development of a segmental coloration, or otherwise. The adsorptive relations of a substance as exhibited in the colloidal state, however, are those of large crystals of that substance, although the effects may be different, and the data of one field is relevant to the other.

Processes usually associated with the colloidal state may be extended to the interaction of true colloids and large crystals. Thus a sol may be coagulated by contact with the oppositely charged surface of an immobile micelle, just as two oppositely charged sols may be coagulated by mixing. Growing crystals may act similarly, and include colloidal or suspended, charged material; the inclusion of colloidal hydrous iron oxide (ordinarily a positive colloid) by amethyst quartz (a negative, immobile colloid by adsorption of OH) is an instance.

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[11] Stranski, I. N., and Kuleliew, K., *Zeits. phys. Chem.*, vol. **142A**, p. 467, 1929.

[12] Serbina, N. N., and Dubinsky, V. G., through *Chem. Abstr.*, vol. **29**, p. 7738, 1935.

[13] Chevalier, J., *Mineral. Mag.*, vol. **14**, p. 142, 1906.

List of Selective Mineral Incrustations

The observed instances of selectivity are tabulated below. The criteria for their recognition are discussed in a later section. A special notation is used to facilitate description of the specimens as follows:

Third formed, selectively incrusting, mineral
First formed mineral—Second formed, selectively incrusted, mineral

Other sequences are indicated by numbers in parenthesis; numbers cited with the localities denote the number of specimens found.

Calcite
(1) Quartz—Dolomite. Cornwall, England; Guanajuato, Mexico (3); Lockport, N. Y.
Dolomite
(2) Pyrite—Rhodochrosite. Alicante, Colorado (2).
Dolomite
(3) Quartz—Calcite. Guanajuato, Mexico (5); Přibram, Bohemia.
Dolomite (3)
(4) Pyrite (1)—Calcite (2)—Goethite (4). Přibram, Bohemia.
Dolomite (4)
(5) Galena (1)—Calcite (2)—Sphalerite (3). Ems, Germany.
Siderite
(6) Quartz—Calcite. Cornwall, England (2); Guanajuato, Mexico (2); Antwerp, N. Y.
Siderite
(7) Pyrite—Calcite. Gilpin Co., Colorado.
Siderite
(8) Galena—Calcite. Neudorf, Germany.
Albite (3)
(9) Microcline—Quartz (2). Pikes Peak region, Colorado (3).
Similarly with quartz earlier than microcline; and with orthoclase in place of microcline, from several localities (4).
Chalcopyrite
(10) Quartz—Sphalerite. Schemnitz, Czechoslovakia.
Chalcopyrite
(11) Galena—Sphalerite. Joplin, Missouri (2).
Chalcopyrite
(12) Dolomite—Sphalerite. Joplin, Missouri.
Chalcopyrite
(13) Siderite—Tetrahedrite. Clausthal, Germany (2).
Chalcopyrite (3)
(14) Tetrahedrite—Dolomite (2). Gersdorf, Germany.

Chalcopyrite
(15) Barite—Quartz—Tetrahedrite. Liskeard, Cornwall.
Similarly, without barite, from Cornwall (2), and Katenik and Přibram, Bohemia.

Tetrahedrite
(16) Quartz—Pyrite—Chalcopyrite. Central City, Colorado.
Similarly, without quartz, from Clear Creek Co., Colorado.

Tetrahedrite
(17) Pyrite—Siderite—Chalcopyrite. Clear Creek Co., Colorado (2).
Similarly, without pyrite, from Horhausen, Germany.

Tetrahedrite
(18) Quartz—Sphalerite. Bohemia

Tetrahedrite (4) Quartz (6)
(19) Quartz—Pyrite—Sphalerite (3)—Dolomite (5). Butte, Montana

Quartz
(20) Sphalerite—Dolomite. Butte, Montana (2).

Quartz
(21) Pyrite—Quartz—Dolomite. Cornwall, England.

Quartz
(22) Specularite—Ankerite. Tavetsch, Switzerland.

Quartz
(23) Pyrite—Rhodochrosite. Alicante, Colorado (2).

Dolomite (3)
(24) Quartz—Galena (2). Raibl, Tyrol.

Dolomite (3)
(25) Quartz—Sphalerite (2). Kapnik, Roumania; Freiberg, Germany.

Dolomite
(26) Sphalerite—Tetrahedrite—Quartz. Ratiborgitz, Bohemia.

Ankerite
(27) Pyrite—Quartz. Brosso, Italy.
Similarly, with quartz earlier than pyrite, from Traversella, Italy (2).

Dolomite
(28) Arsenopyrite—Quartz. Freiberg, Germany (2).
Similarly, with quartz earlier than arsenopyrite, same locality.

Siderite
(29) Microcline—Quartz. Pikes Peak region, Colorado.

Siderite (3)
(30) Quartz—Sphalerite (2). Cumberland, England.

Rhodochrosite (3)
(31) Quartz—Galena (2). Freiberg, Saxony.

Chalcopyrite
(32) Quartz—Dolomite. Cornwall, England; Schemnitz, Czechoslovakia; Schneeberg, and Freiberg, Germany.

Chalcopyrite
(33) Quartz—Calcite. Přibram, Bohemia.

Chalcopyrite
(34) Barite—Siderite. Wildemann, Germany.

Chalcopyrite
(35) Arsenopyrite—Siderite. Freiberg, Germany.

Pyrite
(36) Barite—Calcite. Přibram, Bohemia.
Pyrrhotite.
(37) Quartz—Dolomite. Morro Velho, Brazil (5).
Pyrrhotite
(38) Albite—Dolomite. Minas Geraes, Brazil.
Sphalerite
(39) Fluorite—Siderite. Cumberland, England.
Marcasite
(40) Quartz—Fluorite. Thunder Bay, Lake Superior.
Chalcopyrite
(41) Quartz—Fluorite. Caradon Mines, Cornwall (2).
Pyrite (3)
(42) Fluorite—Quartz (2), Cumberland, England.
Quartz
(43) Galena—Fluorite. Cornwall, England.
Quartz
(44) Pyrite—Fluorite. Isle of Giglio, Italy.
Rutile
(45) Quartz—Specularite. Switzerland (7).
Similarly with quartz later than specularite.
Dolomite (4) Pyrite (3)
(46) Quartz (1)—Pyrrhotite (2). Cornwall, England; Elba, Italy.
Pyrite
(47) Quartz—Barite. Gersdorf, Germany.
Pyrite
(48) Quartz—Galena. Gonderbach, Germany.
Galena
(49) Quartz—Chalcopyrite, Arakawa, Japan.

Discussion of Types of Incrustations

Incrustations Between the Members of the Calcite Group, the Feldspar, and Sphalerite—Tetrahedrite—Chalcopyrite

Approximately one-half of the observed instances of selectivity comprise incrustations between the members of the calcite group (Nos. 1–8), the feldspar group (No. 9), and between sphalerite-tetrahedrite-chalcopyrite (Nos. 10–19). The incrusting and incrusted crystals on all of the specimens were found to be parallely oriented.

While it is not possible to predict in every case on which of several crystal adsorbents the adsorption of a given substance will be strongest, it was early recognized that a crystal adsorbs most strongly substances that are closely related to it in crystal structure. Marc[14] concluded that crystals adsorb substances that are isomorphous with it, and cited the adsorption of rhombohedral sodium nitrate by calcite, and of orthorhombic potassium nitrate by aragonite, but not conversely, as examples. The greater effectiveness of crystal fragments identical or isomorphous with the dissolved substance in inducing the crystallization of supersaturated solutions is a familiar illustration of the rule.

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[14] Marc, R., *Zeits. phys. Chem.*, vol. **75,** p. 710, 1911; vol. **81,** p. 641, 1913.

In the present type of incrustation, the incrusting and incrusted minerals are characterized by an identity or near identity of crystal structure, and the selectivity can be ascribed to a preferential inoculation of a crystallizing solution, by the adsorption of a dissolved, structurally-like, substance. The experimentally obtained selective incrustation of sodium nitrate upon calcite is entirely analogous. It can be expected that the minerals of any isomorphous series, such as those of the barite, aragonite and apatite groups, would form mutual incrustations in preference to other, dissimilar, species.

Incrustations Between Quartz and the Calcite Group.

A number of instances were observed in which quartz incrusted members of the calcite group in preference to other species (Nos. 19–23); also in which minerals of the calcite group selectively incrusted quartz (Nos. 24–31, 46). A mutual affinity for incrustation is also suggested by experimental adsorption data.

The members of the calcite group may selectively incrust quartz, except when another member of the group is also present, as in Nos. 1, 3 and 6, and in several doubtful instances of selectivity not cited in the list. In this case, the earlier carbonate may be incrusted in preference to the quartz. This would indicate that the incrusting affinity between the members of the calcite group is stronger than that of the carbonates for quartz. In most such instances, however, both the quartz and the earlier carbonate are incrusted indiscriminately.

Quartz was not found to incrust another mineral in preference to a carbonate, although many specimens were noted in which the circumstances of association and sequence were such as to make this possible. It was occasionally noted in cases where quartz indiscriminately incrusts calcite, fluorite or barite in company with other species, that the quartz crystals which covered the surface of the former minerals were smaller and more densely aggregated than those which incrusted the adjacent crystals of other species. Such behavior suggests that the deposition of the quartz was affected by the calcite, but that the conditions of deposition were not such as to maintain or establish selectivity.

ADSORPTION OF SILICA BY ALKALINE EARTH COMPOUNDS. The coagulation of silica sols by massive alkaline earth carbonates is well known. Bischoff found that calcite crystals placed in a sodium silicate solution containing CO_2 became covered by a coagulated layer of silica gel, and similar experiments with calcite or aragonite crystals, using dialyzed silica sols or sodium silicate, were described by Thomas Graham and and many others.[15] Gypsum and potassium silicate behave similarly.[16]

A selective deposition of silica upon calcite can be obtained by placing a fragment of this mineral with quartz, sulphides, etc., in a silica sol. The coagulation has been variously regarded as effected by electrolyte, produced by partial dissolution of the calcite (Graham); by direct, hydrolytic adsorption; or by a chemical reaction forming a silicate and CO_2. There is little real distinction to be made between these processes.

Since silica, as such, very probably exists largely in the colloidal state in natural solutions, the observed instances of selective deposition of quartz upon calcite, etc., are presumably exactly represented by the experimental instances.

ADSORPTION OF ALKALINE EARTH COMPOUNDS BY SILICA. The adsorption of electrolytes by quartz suspensions and silica sols has been frequently investigated.[17] In general, the alkaline earth cations are strongly adsorbed by silica, the alkali cations less strongly adsorbed, and the heavy metal cations weakly or negatively adsorbed. The nature of the anion present influences the adsorption to a large extent. Carbonates are adsorbed less strongly than hydroxides, but much more strongly than chlorides, sulphates or nitrates. Bicarbonates are adsorbed less strongly than carbonates. The inorganic acids are not adsorbed and their salts are adsorbed hydrolytically. The alkaline earth hydroxides are very strongly adsorbed, and the presence of (OH) increases the adsorption of the normal salts of the alkaline earth and other cations. The promoting effect is greatest for the alkaline earth cations.

The experimental results with solutions of the alkaline earth hydroxides and powdered quartz indicate a slow reaction between these, with the formation of a hydrated silicate containing adsorbed impurities.[18] The reaction becomes complete at elevated temperatures and as the silica approaches a molecular degree of dispersity. With relatively large quartz particles the reaction is a surface one only (chemosorption).

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[15] Bischoff, G., *Chemical Geology*, vol. **1**, p. 7, 1859; vol. **3**, p. 14, 1863; Graham, T., *Phil. Trans.*, vol. **151**, p. 205, 1861; Gavelle, P., *Chemie et industrie*, vol. **18**, pp. 564–585, 1927; Liesegang, R. E., *Koll.-Zeits.*, vol. **10**, pp. 273–275, 1912; Linck, G., *Koll.-Zeits.*, vol. **33**, p. 274, 1923; Linck, G., and Becker, W., *Chimie der Erde*, vol. **2**, pp. 1–14, 1925; Dean, R. S., *Am. Jour. Sci.*, ser. 4, vol. **45**, pp. 411–415, 1918; Church, A. H., *Jour. Chem. Soc. London*, vol. **15**, p. 107, 1862; vol. **16**, p. 31, 1863.

[16] Becquerel, H., *Compt. rend.*, vol. **36**, pp. 210–211, 1853.

[17] Mattson, S. E., *Koll. Beihefte*, vol. **14**, pp. 227–313, 1922; Pappada, N., and Sadowski, C., *Koll.-Zeits.*, vol. **6**, pp. 292–297, 1910; Mehrotra, M. R., and Dhar, N. R., *Zeits. anorg. Chem.*, vol. **155**, pp. 298–302, 1926; Sallinger, H., *Koll. Beihefte*, vol. **25**, pp. 360–378, 401–412, 1927; Oakley, H. B., *Jour. Chem. Soc. Lond.*, pp. 3054–3065, **1927**; Bartell, F. E., and Ying Fu, *Jour. Phys. Chem.*, vol. **33**, p. 676, 1929; Ahobalacharya, C., and Dhar, N. R., *Jour. Ind. Chem. Soc.*, vol. **9**, pp. 441–453, 1932; Moore, E. S., and Maynard, J. E., *Econ. Geol.*, vol. **24**, pp. 272–303, 365–402, 506–527, 1929.

[18] Baylis, J. R., *Jour. Phys. Chem.*, vol. **32**, pp. 1236–1262, 1928; Patrick, W. A., and Barclay, E. H., *Jour. Phys. Chem.*, vol. **29**, p. 1405, 1925.

In view of this data, adsorption by quartz surfaces in natural alkaline solutions would be such as to favor the super-crystallization of alkaline earth carbonates. Barite and other dominantly alkaline earth compounds can also be expected to have a tendency, to some degree, for deposition upon quartz.

Incrustations Between Quartz and the Metallic Sulphides

Quartz and the metallic sulphides appear either to be without control over the super-crystallization of each other, or to be antipathic in this relation. The latter view, in line with the opinion of Miers,[1] is suggested by certain experimental observations. Instances of quartz selectively incrusting a sulphide or of a sulphide selectively incrusting quartz were not found, although a large number of specimens were noted on which the association and sequence was such as to allow selectivity. These facts do not necessarily indicate that an antipathy for incrustation exists, since the incrusting relation of the associated minerals to the super-depositing quartz or sulphide must be considered, but do suggest the absence of an affinity for incrustation.

Gore[19] found that a number of heavy metal compounds were negatively adsorbed by powdered silica, the solution becoming more concentrated. No adsorption—which may mean an equal adsorption of solute and solvent—or a weak adsorption was observed with other heavy metal compounds, the adsorption in every case being much less than that of alkaline earth and alkali compounds. Mathieu[20] observed that solutions of several metallic salts were negatively adsorbed by porous ceramic plates and capillary glass tubes, and considered that very narrow tubes would adsorb water alone, since the decrease in concentration increased with decreasing radius. It is stated that pure silica gel does not adsorb compounds of the heavy metals directly, but that if the gel has already adsorbed NaOH the Na can be replaced by heavy metal cations.[18]

Negative adsorption of heavy metal compounds would preclude their crystallization upon quartz, except under forced circumstances. Even with a weak adsorption, their selective crystallization upon quartz would probably be prohibited by the stronger, displacing, adsorption of alkaline earth compounds ordinarily present in natural solutions.

Incrustations Between the Metallic Sulphides and the Calcite Group

A number of occurrences were observed in which metallic sulphides had crystallized selectively upon minerals of the calcite group (Nos. 32–39).

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[19] Gore, G., *Chem. News*, vol. **69**, pp. 22–24, 33, 43–46, 1894.

[20] Mathieu, J., *Ann. Physik*, ser. 4, vol. **9**, p. 340, 1902.

Sulphide sols, like silica, are coagulated by contact with carbonates,[21] and selectively so, but there does not appear to be any further experimental or other evidence bearing on the adsorptive relations between these substances.

On many of the specimens it was noted that the deposition of the sulphide was accompanied by the development of solution effects upon the carbonate. This feature suggests that the deposition was induced by the interaction of a solution or sol with the comparatively soluble carbonate. Smyth,[2] in describing his selective incrustation of pyrrhotite upon calcite or dolomite in preference to quartz, remarked that the pyrrhotite occupied solution cavities in the surface of the carbonate, and was inclined to the view that the deposition was caused by chemical reaction with the carbonate.

Tetrahedrite, chalcopyrite and sphalerite were found in a few instances to incrust each other in preference to carbonates. Usually both the earlier sulphide and the carbonate are incrusted without selectivity. The selectivity in these instances illustrates on a hand-specimen scale the tendency of limestone formations to localize deposition from traversing ore solutions. Selective incrustations of carbonates upon sulphides were not noted, although many specimens were observed in which this was feasible. The metallic sulphides are probably without any marked control over the crystallization of the minerals of the calcite group.

Miscellaneous Incrustations

A few instances of selectivity remain which have not been previously discussed (Nos. 40–49).

Of these, the selective incrustations of chalcopyrite, pyrite and marcasite upon fluorite (Nos. 40–42) may have originated by the interaction of a sol or solution with the fluorite, as with the sulphide incrustations upon the carbonates, in view of the relatively high solubility of this species. Sulphides can apparently incrust carbonates in preference to fluorite, from the evidence of No. 39 and of a few doubtful instances of selectivity, not cited in the list. The selective incrustations of quartz upon fluorite (Nos. 33, 34) are probably similar in origin, and can be classed with the incrustations of quartz upon the calcite group.

The selectivity in the remaining instances can not be correlated with any particular known adsorptive relation. The incrusting and incrusted minerals are seen to be mutually oriented in the selective incrustations of rutile upon specularite (No. 45) and of pyrite upon pyrrhotite (No. 46), so that adsorption has evidently operated in their formation. Sulphide sols may be selectively coagulated by contact with massive sulphides.[22]

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[22] Rust, G. W., *Jour. Geol.*, vol. **43,** p. 419, 1935.

[21] Tolman, C. F., and Clark, J. D., *Econ. Geol.*, vol. **9,** p. 577, 1914.

FACTORS INFLUENCING THE RECOGNITION AND PRESERVATION OF SELECTIVITY

It is obviously a requisite for the existence of selectivity that the incrusting mineral be crystallizing in the presence of drusy crystals of at least two other species of earlier formation. Recognition of selectivity thus requires an exact determination of the sequence of deposition. Many incrustations which on casual examination appear to be selective are eliminated by a study of sequence. Particular difficulties are often encountered when the seemingly selectively incrusted mineral is the first formed of the sequence.

The recognition of selectivity is influenced by the ratio of size of the incrusting and incrusted crystals. Selectivity is most apparent when the crystals of the earlier formed minerals are large and the crystals of the incrusting mineral are small and abundant. The crystals of the several species available for incrustation should also be about the same size and equally distributed over the specimen. Uncertainty as to the validity of selectivity arises in specimens on which the incrusting mineral forms a few scattered crystals only, or where the incrusted mineral forms the greater part of the specimen and the non-incrusted mineral is present as a few small crystals only. Most of the doubtful instances of selectivity observed were of this nature.

Many instances were also noted in which the last formed mineral, while dominantly incrusting one of the earlier formed species, was also present as a few scattered crystals upon the associated minerals. A record kept of these occurrences, and of the doubtful occurrences, none of which are included in the list given, showed that they conformed closely to the types of incrusting behavior as recognized.

Although the tendency for selective incrustation is a general one, unequivocable examples of selectivity are not common. In part, this is due to the infrequency with which the fortuitous conditions of association and sequence requisite for the manifestation of selectivity on a hand-specimen scale are satisfied. More generally, the development and preservation of selectivity requires conditions of crystallization which are probably rarely satisfied in natural solutions.

The control of crystallization solely by adsorbing interfaces present in the solution would be favored by slow crystallization from quiet solutions which did not contain suspended nuclei. Deposition from natural solutions, however, may be characterized by more or less hurried crystallization from moving solutions that contain transported, suspended nuclei. Rapid crystallization also tends to form free nuclei within the solution as well as at interfaces. The mechanical lodging of such nuclei upon drusy crystals would obscure a tendency for selectivity under adsorption control by setting up numerous accidentally placed centers of crystallization.

Further, the preservation of selectivity requires that the incrusting mineral be not deposited in amount greater than that just sufficient to cover the selectively incrusted crystals. An incrustation that is selective in an early stage of its development may have the selectivity obscured by the continued growth and lateral spreading of the incrusting mineral.

SUMMARY

The crystallization of one mineral upon another in the formation of a mineral incrustation is, in general, influenced by adsorption at the boundary between the incrusted crystal and the solution.

When a mineral crystallizes in the presence of drusy crystals of several earlier formed species, adsorption may induce the selective incrustation of one of the species. Chemical reaction between a solution or sol and the surface of the incrusted crystal (chemosorption) may also effect selectivity.

In the present study, instances of incrustations selective between minerals are described, and the incrusting relations of several groups of common minerals are discussed in light of such evidence and of experimental adsorption data. It is found that:

(1) Minerals which are identical or nearly identical in crystal structure, such as the members of the calcite group, the feldspars, and sphalerite—tetrahedrite—chalcopyrite, have a marked tendency to incrust each other in preference to other species.

(2) Quartz and the members of the calcite group have a tendency for crystallization upon each other. The tendency for crystallization of a carbonate upon quartz is less strong than that for crystallization upon a related carbonate.

(3) Quartz and the metallic sulphides either are without a tendency for crystallization upon each other or, more probably, are antipathic in this relation.

(4) The metallic sulphides have a tendency for crystallization upon the minerals of the calcite group and upon fluorite. Sulphides appear to incrust carbonates in preference to fluorite, and sphalerite—tetrahedrite—chalcopyrite may incrust each other in preference to carbonates. The sulphides are probably without control over the crystallization of the minerals of the calcite group.

THE UNIT CELL AND SPACE GROUP OF CUBANITE

M. J. BUERGER, *Massachusetts Institute of Technology, Cambridge, Mass.*

ABSTRACT

Sudbury cubanite has been studied by the equi-inclination Weissenberg method. This investigation leads to the following information:

Centrosymmetrical symmetry:	$mmm=D_{2h}$	
Crystal system:	orthorhombic	
Unit cell:	*absolute*	*ratio*
	$a=$ 6.43 Å	.582
	$b=$ 11.04	1.000
	$c=$ 6.19	.561
	$z=4$ $CuFe_2S_3$ per cell	
Diffraction symbol:	$mmmPc-n$	
Space group:	Pna $(=C_{2v}^9)$, or $Pcmn$ $(=D_{2h}^{16})$.	

The axial ratio chosen by surface morphological study is referred to the correct structural cell.

INTRODUCTION

Peacock and Yatsevitch[1] have recently made a well coördinated study of cubanite from the Frood Mine, Sudbury, Ontario. The writer is indebted to Dr. Peacock and also to Professor Palache of Harvard University for the privilege of basing the present structural study on this well described material. The characteristics of this cubanite are as follows:

orthorhombic holohedral
$a:b:c=.5822:1:.5611$
axis of high magnetic susceptibility: [010]
$d^{27}=4.101$
analysis:

Cu	22.88%
Fe	41.41
S	35.35
	99.64

Some difficulty was experienced in obtaining a single crystal free from twinning and still having a sufficiently full form development to permit it to be easily oriented for rotations about the three crystallographic axes. A specimen was finally selected which was obviously a twin, but in which the twin boundary could be recognized. From this a rough small piece was removed which contained only one individual, and which was bounded by a few recognizable planes.

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[1] Peacock, M. A., and Yatsevitch, G. M., Cubanite from Sudbury, Ontario: *Am. Mineral.*, vol. **21**, pp. 55–62, 1936.

CELL CHARACTERISTICS

METHOD. The entire study was carried out by the equi-inclination Weissenberg method.[2] A specially constructed equi-inclination apparatus was used for this purpose.[3] The films were interpreted by the new inspective method,[4] without any indexing.

The cell characteristics were determined from films taken with the use of cobalt radiation, which is only slightly absorbed by iron bearing crystals and which is quite clean. These films include ordinary rotation photographs about each of the three crystallographic axes (the second two being superfluous except as checks on orientation and cell dimensions), Weissenberg resolutions of the equators of each of these rotations, and equi-inclination resolutions of the 1st, 2nd and 3rd layers for the c axis rotation, as well as the 3rd layer for the a axis rotation (chiefly for symmetry).

For the determination of parameters, it is desirable to have reflections of higher orders than can be recorded by the long wave-length cobalt radiation. Accordingly, a second set of equatorial Weissenberg photographs was made for the three axial rotations, using molybdenum $K\alpha$ radiation (zirconia screened).

SYMMETRY. The equi-inclination Weissenberg photographs for rotations about the three crystallographic axes, regardless of layer, are all equi-inclination projections of the plane symmetry C_{2l}. This fixes the centrosymmetrical point-group of the crystal as $mmm = D_{2h}$, and fixes the crystal system as orthorhombic, a conclusion in accord with the results of study of the surface morphological development of cubanite.

The equatorial photograph for the c axis rotation displays a pseudo-symmetry extraordinarily close to C_{6l}, but the n layer photographs for the same rotation axis entirely lack this pseudo-symmetry. This plainly indicates that the crystal structure projected on the (001) plane is based upon some hexagonal framework.

SPACE LATTICE TYPE. The c axis 1st, 2nd, and 3rd layer equi-inclination photographs are all of type 11, corresponding with rectangular plane lattices having a point at the rotation axis. All photographs, when superposed, show an identical distribution of spots. The stacking sequence is therefore 9, coincident rectangles. This information together with the symmetry previously noted, fixes the space lattice type as primitive orthorhombic, $mmmP$.

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[2] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Zeits. Krist.* (A), vol. **88**, pp. 356–380, 1934.

[3] Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Zeits. Krist.* (A), vol. **94**, pp. 87–99, 1936.

[4] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeits. Krist.* (A), vol. **91**, pp. 255–289, 1935.

UNIT CELL. The cell dimensions were first roughly determined from the layer line spacing of the c axis rotation, plus Z measurements of the dome reflections on n layer equi-inclination photographs for the c axis rotation. These values were subsequently refined by X measurements of high order pinacoid reflections. The cell so determined is as follows:

Absolute	Ratios	
	Cell (Buerger)	Surface Morphology (Peacock and Yatsevitch)[1]
$a=$ 6.43Å	$.582_5$	.5822
$b=$11.04	1.	1.
$c=$ 6.19	.561	.5611
	$\frac{a}{c}=1.038$	1.038

The cell contents are obtained through the use of the relation:

$$\text{density} = \frac{\text{cell mass}}{\text{cell volume}} = \frac{N \times f \times 1.649 \times 10^{-24}}{V} \tag{1}$$

where N = the number of formula weights per unit cell
f = the formula weight.

The chemical analysis may be reduced as follows:

	Weight per cent	Atomic per cent	Atomic ratios	Excess for ideal $CuFe_2S_3$
Cu	22.88	3.600	.980	$-.020$
Fe	41.41	7.415	2.018	$+.018$
S	35.35	11.025	3.000	.000

It will be observed that the analysis indicates an excess of iron over that required by the ideal formula $CuFe_2S_3$. This excess is almost exactly balanced by a copper deficit. It is fairly apparent, therefore, that the analysis indicates that one metal is substituting for the other in proxy solid solution.[5] Without pushing the precision of the analysis too far, the formula for the Frood cubanite may thus be written[6]

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[5] Buerger, M. J., The pyrite-marcasite relation: *Am. Mineral.*, vol. **19**, pp. 53–58, 1934.

[6] Buerger, M. J., The temperature-structure-composition behavior of certain crystals: *Proc. Nat. Acad. Sci., U.S.A.*, vol. **20**, p. 446, 1934.

$$\left|\begin{matrix}Cu_{.98}\\ \\ Fe_{.02}\end{matrix}\right| Fe_2S_3$$

This has a formula weight of 271.3 as compared with 271.4 for the ideal compound.

Substituting this value of the formula weight, the cell volume, and the measured[1] density, 4.101, in relation (1) above, leads to a 4.02_5 formula weights per unit cell.

SPACE GROUP. Comparison of the reciprocal translations on the three zero layer photographs, with the reciprocal translations of the lattice as shown by the *n* layer photographs, reveals the following multiple translations in the zero levels of the reciprocal lattice:[4]

plane	doubled reciprocal translation
(100)	*c*
(010)	none
(001)	*a* and *b*

Some of the above space pattern characteristics were checked by Mr. Ely Mencher who graphically reconstructed[2] the reciprocal lattice.

These multiple translations indicate the following symmetry characteristics:

plane	glide components
(100)	$\frac{c}{2}$
(010)	----
(001)	$\frac{a}{2}+\frac{b}{2}$

The diffraction symbol is therefore *mmmPc-n*. This diffraction effect may be obtained from either of the space groups *Pcmn* (D_{2h}^{16}), or *Pc-n*, which transforms by axial interchange to *Pna-*=*Pna* (Mauguin) ($=C_{2v}^{9}$).

ACKNOWLEDGMENT. The writer is indebted to the International Nickel Co., Ltd., for permission to publish this study.

NOTES AND NEWS

A BOMB FOR USE IN HYDROTHERMAL EXPERIMENTATION

George W. Morey and Earl Ingerson, *Geophysical Laboratory, Carnegie Institution of Washington.*

There is much interest in the decomposition and synthesis of minerals by water at high temperatures and pressures, and a simple and reliable type of bomb is needed for the study of such reactions. The bomb described by Morey and Fenner[1] has been used by other investigators, and

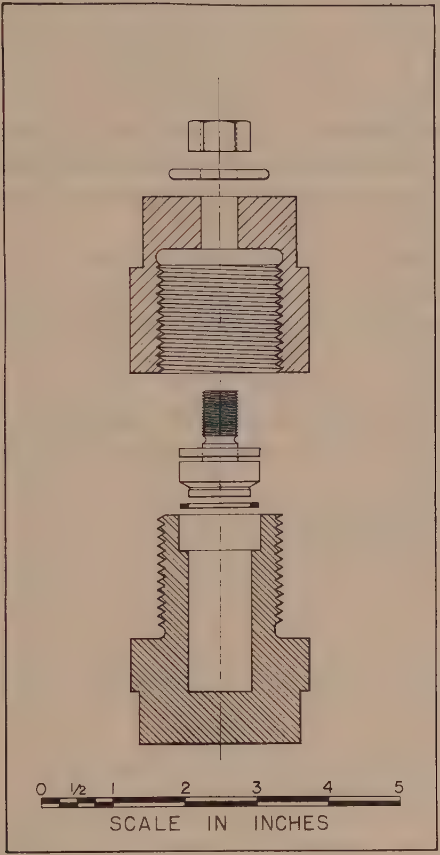

Fig. 1. Bomb for use in hydrothermal experimentation. The body of the bomb and the plunger are made of stainless steel; the screw cap, of tool steel. The washer that effects the seal (shown in black) is of annealed copper.

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[1] *Jour. Am. Chem. Soc.*, vol. **36**, p. 215, 1914.

is still used by us for some work. For most experiments, however, we have found the smaller type of bomb described herewith to be more convenient.

The new bomb is shown in the figure, drawn to the scale indicated. We have found that stainless steel is not suitable for both the body of the bomb and the screw cap, because of its tendency to "freeze." The threads in a tool-steel bomb, such as was previously used, quickly become hardened by the graphite and oil lubricant so that seizure never becomes troublesome below about 700°, but with stainless steel the surfaces remain almost unaltered, and at temperatures as low as 500° it is difficult to prevent seizure. Accordingly we have adopted the practice of making the body out of stainless steel,[2] and the screw cap out of tool steel.[3] The plug is of the same stainless steel, which gives a chamber consisting entirely of this material. The friction washer, placed between the shoulder of the plug and the screw cap, is of monel metal. The closure is effected by a copper washer, shown in black.

Temperature is measured by a thermocouple, placed in a 3/16″ hole (not shown) drilled in the plug to within about $\frac{1}{4}$″ of the bottom. In some experiments a hole has been drilled entirely through the axis of the plug, the top of which is provided with a fitting to connect to a cylinder of carbon dioxide.

This type of bomb is more convenient to use than the larger type previously described, and has given complete satisfaction.

[2] Carpenter's Stainless No. 8.

[3] Halcomb's Ketos oil hardening steel.

SUPPLEMENTARY NOTE ON CHALCOMENITE

Charles Palache, *Harvard University, Cambridge, Mass.*

The author has had the privilege, through the kindness of Professor J. D. H. Donnay, of examining the notebooks and measured crystals left by the late Dr. H. Ungemach. Among these crystals are three of chalcomenite from a third locality, Sierra de Umango, Argentina. Ungemach had adopted for these crystals, elements corresponding to those proposed by me in a recent paper.[1] His values differ slightly:

	Ungemach	Palache
$a:b:c$	0.7274:1:0.7998	0.7325:1:0.8077

He found the forms (010), (101), (120), (110), (011) and (111), all reported by me; and two additional forms (112) and (121). I remeasured Ungemach's best crystal and confirmed all his forms including the new ones.

	Measured		*Calculated*	
	ϕ	ρ	ϕ	ρ
h(112)	54°37′	34°30′	53°46½′	34°21′
k(121)	35 18	63 57½	34 19	62 55

The measurements are, on the whole, inferior to those obtained on the Hiaco crystals; the distribution of faces, however, confirms the sphenoidal symmetry found in my work.

I feel it a pleasant duty to put on record this prior determination by my valued friend of the true symmetry of this rare species. Dr. Ungemach's notes covering several thousand crystals of hundreds of minerals are rich in observations which it is hoped may in large part be published from time to time.

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[1] Palache, Charles, Chalcomenite from Bolivia; *Am. Mineral.*, vol. **22**, pp. 790–795, 1937.

ON THE ORIGIN OF MONTMORILLONITE

W. Harold Tomlinson and Adolph E. Meier,
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The rock bentonite, the principal source of montmorillonite for experimental purposes, was shown by D. F. Hewett[1] and by E. T. Wherry[2] to be a leached and hydrated volcanic ash. Montmorillonite has also been described as having been derived from the decomposition of pegmatite[3] and from spodumene.[4] Ewell and Insley[5] prepared montmorillonite synthetically in 1935. Recently W. Noll[6] described an elaborate series of experiments made at Hanover, in which he prepared montmorillonite synthetically from mixtures of alumina, silica, water and various bases, of which magnesium hydrate proved to be the most effective. Noll believed that the conditions under which his experiments were performed would be equivalent to conditions of surface weathering extended over a longer period of time.

The authors have come upon a clay mineral at Glen Riddle, Delaware County, Pennsylvania, which has proved to be montmorillonite and which is evidently in process of formation in position, where found. The natural processes of surface alteration in operation at this locality, are easily determined. Solid rock can be found blending into clay. The alteration of plagioclase can be traced in all stages, from fresh unaltered albite oligoclase to montmorillonite replacement and to montmorillonite in veins.

This montmorillonite is found in roughly horizontal joint-seams across a thin tongue of gabbroid material, and as an alteration product of plagioclase in the wall rock adjacent to these seams. The tongue of gabbroid material as exposed makes contact with a meta-pyroxenite. It is granular in texture, medium in grain size and has a gneissic structure which parallels its irregular contacts. Its mineral composition varies. Where the montmorillonite is found, albite-oligoclase is the chief feldspar and biotite the chief ferro-magnesian mineral. Barium feldspar is present and also cassinite, an intergrowth of albite-oligoclase and a barium-potash feldspar.

When freshly dug this clay breaks into translucent lumps with a pale greenish color. Upon drying it becomes white and of granular appearance. When dropped into water, the partially dried clay expands rather violently. Examined optically much of this clay shows low birefringence, being practically amorphous with an index sharply lower than balsam. Where the clay shows crystallization both indices are sharply below the balsam and the birefringence is sufficient to give a first order red in the thicker flakes. We have not found material sufficiently coarse for a satisfactory study of the indices. The 1.47 liquid comes nearest the fine grained material.

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[1] *Jour. Wash. Acad. Sci.*, vol. **7,** p. 196, 1917.

[2] *Jour. Wash. Acad. Sci.*, vol. **7,** p. 576, 1917.

[3] Analysis given in "*Clays*" (3rd ed.), H. Ries, p. 72.

[4] *Am. Jour. Sci.*, vol. **20,** p. 283, 1880.

[5] *Jour. Research Nat. Bur. Standards*, **RP 819,** vol. 15, Aug. 1935.

[6] *Min. u. Pet. Mitt.*, Band **48,** Heft 3–4, 1936.

A chemical analysis of a sample made without preliminary drying shows a composition as indicated in column "A" of Table 1. When calculated to a water free basis, after 15.5 per cent water had been driven off at 110°C, the analysis is shown in column "B".

Table 1. Chemical Analysis of Glen Riddle Montmorillonite

	A	B	Molecular Proportions	Molecular Ratios	Molecular Ratios in Whole Numbers
SiO_2	48.79	57.74	.961	$4 \times .240$	12
Al_2O_3	20.73	24.53	.240	$1 \times .240$	3
MgO	5.40	6.39	.159	$\frac{2}{3} \times .240$	2
CaO	0.38	0.45	.008	—	—
Alkalies*	0.80	0.94	.015	—	—
Total H_2O	23.74	—	—	—	—
$H_2O+110°C$	—	10.24	.569	$2\frac{1}{2} \times .240$	7
$H_2O-110°C$	(15.50)	—	—	—	—
Total	99.84				

* Alkalies reported as Na_2O. Total alkalies only were determined.

A. Analysis of sample without previous drying at 110°C.

B. Calculated to moisture free basis at 110°C.

The water-free composition as expressed in column "B" leads to the formula $2MgO \cdot 3Al_2O_3 \cdot 12SiO_2 \cdot 7H_2O \cdot Aq$. Dana quoting LeChatelier gives the formula for montmorillonite, $H_2Al_2Si_4O_{12} \cdot nH_2O$.[7] Ross and Shannon[8] gave the formula as $(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$, but decided later that there should be only 4 silica molecules. Noll[6] in his experimental work used an alumina to silica ratio of 1:4.

This montmorillonite showed the following water loss on heating:

At 110°C. for 12 hrs.	15.5 %
At 140° for 17 hrs.	16.5
At 190° for 4 hrs.	17.8
At 240° for 3 hrs.	18.3
At red heat	23.74

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[7] *System of Mineralogy.* (6th ed.)

[8] *Jour. Am. Cer. Soc.*, vol. 9, p. 77, 1926.

The hill on the flank of which this montmorillonite is found, is made up largely of a thoroughly serpentinized meta-pyroxenite. At the surface and to a considerable depth, this is in an advanced stage of decomposition. Any meteoric waters reaching the joint seams in which the montmorillonite occurs, must first pass over or through this decomposing meta-pyroxenite. That such waters would pick up magnesium salts is a reasonable supposition. That these waters actually have picked up and transported magnesium salts is indicated by the abundant presence of hydrous magnesium silicate minerals with the montmorillonite (Fig. 1).

If we examine sections across one of these veins and into the solid wall rock, we find that the solutions traversing the seam have made a strong attack on the albite-oligoclase along the wall, altering it to montmorillonite. This alteration may extend for several inches into the wall rock. The most interesting feature of this reaction is the fact that the magnesian solutions attack the plagioclase readily without appreciably affecting the other feldspars in the rock. We have prepared a photomicrograph (Fig. 2) to illustrate this selective action. In this photograph differences in relief have been accentuated by a photographic deception so that the montmorillonite appears a deep grey and the unaltered feldspars white. The large grains with platy structure represent cassinite. So selective is this alteration that the albite-oligoclase plates have been thoroughly altered to montmorillonite, the alternate plates of barium-potash feldspar remaining unattacked. This selective action was observed in all sections prepared from material taken adjacent to one of the montmorillonite veins.

At this locality the authors find montmorillonite to be forming from an attack of magnesium solutions on a plagioclase of about the composition Ab_6An_1. We believe this locality gives field evidence for the genesis of montmorillonite, confirming the conclusions reached by Noll from his laboratory experiments.

The reaction expressing this change as based on field evidence seems to be as follows: Plagioclase (appr. Ab_6An_1), plus basic magnesium carbonate, plus water, equals montmorillonite, plus calcium carbonate, plus sodium carbonate (the last two salts removed in solution).

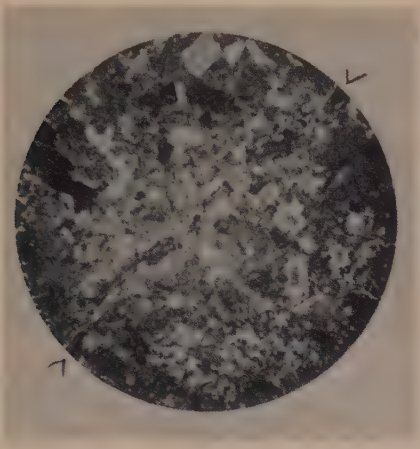

FIG. 1. Hydrous magnesium silicate minerals cutting through montmorillonized rock. Cr. nicols. ×30.

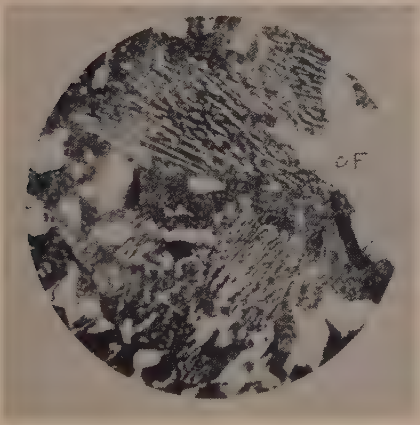

FIG. 2. Albite-oligoclase altered to montmorillonite (grey). Other feldspars unattacked (white). ×30. One nicol. OF = open field.

A NEW MICROCHEMICAL TEST FOR SELENIUM

M. Harrison Evans, *California Institute of Technology, Pasadena, California.*

In the course of an investigation of microchemical methods as applied to the identification of minerals, the writer has found a test for selenium that does not seem to have been described heretofore. The test appeared to be so highly satisfactory that it was worked out in detail to find the conditions under which the reaction took place and the possible interference that might be caused by the presence of other elements in the test solution.

A number of tests for selenium have been described and are in general use. The most widely used test depends on the precipitation of the element from a hydrochloric acid solution by addition of stannous chloride solution.[1] The product is a brick-red, amorphous precipitate of selenium. This test is sensitive and characteristic but unfortunately the reagent will also precipitate tellurium, gold and mercury, and these may obscure the selenium. Another test for selenium uses potassium iodide to precipitate a reddish-brown powder of selenium iodide.[2] It has been found, however, that a number of elements, notably tellurium, copper and gold, also give precipitates with potassium iodide and that the products are sometimes indistinguishable from the selenium reaction.

The new test, using the organic compound, thiourea ($SC(NH_2)$), has the advantage that the very highly colored product is distinctive and by observing certain precautions hereafter described, it is specific and not interfered with by other elements in the test solution. The test is made in cold, dilute hydrochloric acid solution by adding a drop of 10 per cent thiourea solution in water to a drop of the test solution on a glass slide. On adding the reagent, long streamers of a fine, amorphous, brilliantly red precipitate slowly spread across the drop. By transmitted light the precipitate ranges in color from very dark blue to purplish red, but by directing the light source onto the top of the slide the characteristic brilliant red color can be seen. The appearance of this precipitate is very characteristic under the microscope and can be recognized in concentrations down to less than 0.01% Se, but it is so highly colored that in most cases it will be plainly visible to the unaided eye.

Of all the common elements tested, only copper, gold, mercury and bismuth react with the reagent or interfere with the selenium test. Copper produces a precipitate with thiourea which is white by reflected light and dark brownish by transmitted light. Mercury produces a colorless, crystalline precipitate. Bismuth forms a clear, yellow solution with thiourea. Gold forms an immediate blue-black precipitate which redissolves and does not interfere further. These reactions are seldom strong enough to mask the brightly colored selenium precipitate, but interference by these elements can be largely obviated by the following procedure.

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[1] Short, M. N., *Microscopic Determination of the Ore Minerals, U. S. Geol. Survey, Bull.* **825,** 1931.

[2] Short, M. N., *idem.*

A minute fragment of the mineral to be tested is broken down on a glass slide with a drop of 1:1 HNO_3. Part of the selenium in the mineral is precipitated as the element in a red, glutinous mass or a red powder which is not attacked by HNO_3, HCl or aqua regia. The rest of the selenium is deposited as a white residue of H_2SeO_3. This is sparingly soluble in 1% HNO_3 and H_2O, distinctly more soluble in 1:7 HNO_3, and readily soluble in 1:5 HCl. Leach the residue from the decomposition with 1% HNO_3 to remove copper and finally with a drop of water, removing both drops. Then leach with a drop of cold 1:5 HCl, transfer the drop and test with thiourea for selenium.

The same procedure will also eliminate mercury from the residue although most mercury compounds must be broken down with aqua regia. If the mineral is not decomposed by 1:1 HNO_3, aqua regia is used and the residue is leached as above with 1% HNO_3, thus removing mercury.

Bismuth reacts with thiourea to form a clear, yellow solution. The reaction is sensitive enough that it has been recommended by Watson as a spot test for bismuth.[3] The character and color of the product is so different from the selenium reaction that bismuth will not mask even very small amounts of selenium. Selenium will mask bismuth but if the test drop is filtered or allowed to settle, both elements can readily be recognized in the presence of one another.

Gold, as noted above, forms a precipitate with thiourea but this redissolves in excess thiourea and there is no further color reaction and no interference with the selenium reaction. Moreover, gold is also eliminated from the test solution under the procedure given above for preparing the solution.

The following elements were tested in 1% solutions to determine their reactions with thiourea and the effects they might have on the selenium reaction: As, Au, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Sn, Te, Ti, and Zn. Mercurous mercury and silver cannot appear in the hydrochloric acid solution. With the exceptions noted above, none of these elements interferes. Moreover, it should be remarked that the selenium precipitate is the only intensely colored reaction given by any of the common elements with thiourea. Thus, selenium can be detected even in the presence of large amounts of copper, mercury or bismuth. The greatest advantage of the test, aside from its extreme sensitivity, is the fact that the product with selenium is wholly dissimilar from that given by any other common element.

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[3] Watson, J. Adam, Colour reactions in the micro-chemical determination of the elements: *Mineral. Mag.*, vol. **24**, pp. 21–34, 1935.

This test appears much more satisfactory to the writer than either of the common microchemical tests used in mineragraphic identification. Both stannous chloride and potassium iodide precipitate many elements whose products may obscure one another, whereas this reaction is very sensitive, the colored product is unique, and it can be made specific. The nature of the precipitate is not known but it is presumed to be a complex organic compound since it is quite different from the elemental selenium precipitate produced by stannous chloride.

Contribution **234**.
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PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences of Philadelphia, April 1, 1937

Mr. Arndt presided at a stated meeting, with 39 members and 35 visitors present. Messrs. Richmond E. Myers, John S. Penny, and George R. Cope were elected to membership.

Participation in the Hobby Show at the Commercial Museum, May 10th to 15th, with exhibits of mineral specimens, was approved. Mr. Morrell G. Baldwin spoke on "Ancient and Medieval Gemology."

Albert Jehle reported malachite and quartz crystals from Bridgeport, and Edwin Roedder exhibited thorianite, gummite, and uranophane from Easton, and jeffersonite and calcite from Franklin, New Jersey.

May 6, 1937

A stated meeting was held with Mr. Arndt in the chair, 49 members and 33 visitors were in attendance. The deaths of J. Rady Miller, and Fred Hilbiber were announced.

Dr. J. D. H. Donnay, assisted by Dr. David Harker, of Johns Hopkins University, addressed the society on his new law of crystallography, which is a further development of the Law of Bravais. The use of perforated cards (representing properties of minerals) in the determination of non-opaque minerals was demonstrated.

A number of trips were reported, and many specimens were exhibited: W. H. Flack, collected at Easton, Pa. (aragonite, asbestos, eastonite, gummite, thorianite, uranophane); Leonard Morgan, at Bernardsville, N. J. (natrolite); at Prospect Park, N. J. (amethyst, chabazite); George R. Cope, at Unionville, Pa. (chesterlite, beryl, corundum); Samuel G. Gordon, at Grafton, N. H. (apatite, uraninite, uranophane, autunite); Edwin Roedder, at Unionville, Pa. (beryl); Louis Moyd, at Sparta, N. J. (allanite).

June 3, 1937

Mr. Arndt presided at a stated meeting with 49 members and 27 visitors present. Albert Jehle was elected to junior membership, and Joseph Berman to senior membership.

Vice-president Joseph L. Gillson described his "Rambling in the Southwest," with descriptions of the fluorspar deposits of New Mexico, and the titaniferous magnetite deposits of the San Gabriel Mountains in California.

Dr. H. E. McKinstry discussed the distribution of metamorphic minerals in southeastern Pennsylvania, particularly in the Wissahickon gneiss. He requested that members report occurrences of garnet, staurolite, cyanite, and sillimanite in the area between the Delaware River and the Susquehanna.

A number of trips were reported: Albert Jehle and Leonard Morgan, collected at Ellenville, N. Y. (quartz, galena), at Hudson, N. Y. (fluorescent and phosphorescent selenite); Louis Moyd, at Chimney Rock, N. J. (calcite); Edwin Roedder, at Media, Pa. (a feldspar crystal).

W. H. Flack, *Secretary*

NEW MINERAL NAMES

Arsenostibite

P. Quensel: Minerals of the Varuträsk Pegmatite. III. Arsenostibite, a hydrous oxidation product of allemontite. *Geol. Fören. Förhandl. Stockholm.*, vol. **59**, pp. 145–149, 1937.

Chemical Properties: A hydrous oxide of antimony and arsenic, $(R_2O_3, R_2O_5)\cdot 3H_2O$. Analysis: Sb_2O_5 45.4, As_2O_5 5.8, Sb_2O_3 4.3, As_2O_3 5.6, Fe_2O_3 6.2, Bi_2O_3 0.3, CuO 0.0, H_2O- 8.1 H_2O+ 6.6, insol. 18.1; Sum 100+.

Physical Properties: Color, sulfur-yellow. Isotropic, with index of refraction variable, 1.670–1.685.

Occurrence: Found as a porous coating, an alteration of allemontite from the pegmatite at Varuträsk, Sweden.

W. F. Foshag

Alpha-wiikite

Beta-wiikite

Jalo Ant-Wuorinen: Der Wiikite und Seine Chemische Zusammensetzung. 2d Mitt. *Bull. Com. Geol. Finlande*, No. **115**, pp. 213–229, 1936.

Wiikite is interpreted as an isomorphous mixture of (1) Alpha-wiikite, $3CaO\cdot UO_3\cdot 1.5 Cb_2O_5\cdot 1.5\ H_2O$ and Beta-wiikite, $2Y_2O_3\cdot 1.5\ Cb_2O_5\cdot 1.5\ H_2O$.

W. F. F.

NEW DATA

Tuhualite

P. Marshall: The mineral tuhualite. *Trans. Proc. Roy. Soc. N. Z.*, vol. **65**, pp. 330–336, 1936, 11 text figures.

Chemical Composition: Analysis (by Mrs. F. T. Seelye) (calculated from rock analyses), SiO_2 75.36, Al_2O_3 9.33, Fe_2O_3 3.61, FeO 2.33, MgO 0.06, CaO 0.25, Na_2O 4.75, K_2O 4.06, H_2O- 0.21, H_2O+ 0.12, TiO_2 0.23, MnO 0.18; Total 100.16.

Crystallographical Properties: Orthorhombic. $a=0.915$, $c=0.512$. Habit prismatic. Forms: (100), (010), (001), (110), (111), (011), (021). $a\wedge m=42.3°\pm 1.5°$, $c\wedge(011)=37.4°\pm 0.6°$. Sometimes twinned, with brachydome as the twinning and composition plane.

Physical and Optical Properties: Color black to very dark blue; luster submetallic. Pleochroism strong. $X=a$, palest pink, $Y=b$, purple; $Z=c$, deep violet. $\alpha=1.601$, $\gamma=1.607$. Birefringence moderate. Biaxial, negative, $2V=65°-70°$. Dispersion $r>v$. Cleavages basal, macropinacoidal and brachypinacoidal, good. G. 2.87.

Alteration: Frequently altered to a greenish yellow mineral; pleochroic, $X=$pale yellowish green, $Z=$deep olive green. Habit flaky. Biaxial, $2V$ large. Birefringence 0.01; lamellar twinning common with symmetrical extinction angles of 20°–24°.

W. F. F.

List of Errata

The following misprints appeared in the May issue:

p. 520, line 16 from top, read "enargite," instead of "energite."
p. 569, last line of footnote, read "β 1.584," instead of "β 1.548."
p. 586, in Table, read "Beryl," instead of "Bery."
p. 605, line 6 from top, read "Schaller," instead of "Scaller."
p. 663, line 11 from top, read "$2Ag_2S$," instead of "$2Ag_4S$."
p. 720, under Fig. 1, read "Almandine," in place of "Alamandine."
p. 722, Table 2, column 3 (for Fe_2O_3, read "1.50," instead of "1.55." Column 5, summation should read "100.25," instead of "10.25."
p. 726, Table above Fig. 3, under Pyroxmangite, read "γ 1.764," instead of "γ 1.746."
Under Iron Rhodonite, read "$2V_\gamma$ 37°," in place of "$2V_\gamma$ 27°."